

PATENT ABSTRACTS OF JAPAN

(11)Publication number:

2000-323276

(43) Date of publication of application: 24.11.2000

(51)Int.CI.

H05B 33/10

G09F 9/30

H05B 33/12

H05B 33/14

H05B 33/22

(21)Application number: 11-134320

(71)Applicant: SEIKO EPSON CORP

(22)Date of filing:

14.05.1999

(72)Inventor: SEKI SHUNICHI

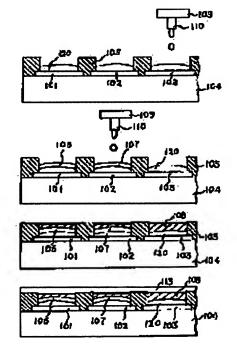
KIGUCHI HIROSHI

(54) MANUFACTURE OF ORGANIC EL ELEMENT, ORGANIC EL ELEMENT, AND INK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide the manufacturing method of an organic EL (electroluminescente) element comprising an organic stacked film with low cost and high characteristics and provide an ink composition capable of manufacturing this organic EL element.

SOLUTION: This manufacturing method of an organic EL element having structure interposing a hole injection layer 120 and an luminescent layer 106 with an anode 101 and a cathode 113 has a process in which a hole injection layer 120 is formed by applying an ink composition containing a hole injection material made of an organic compound to a specified region on a substrate by an ink jet method; and a process in which luminescent layers 106, 107 are formed by applying an ink composition containing a luminescent material made of an organic compound by an ink jet method.



LEGAL STATUS

[Date of request for examination]

06.10.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

JAPANESE [JP,2000-323276,A]
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the organic EL element characterized by to provide the process which applies the ink constituent containing the hole-injection material which is the manufacture method of the organic EL element of structure of having ****(ed) the hole-injection layer and the luminous layer by the anode plate and cathode, and becomes a predetermined field on a substrate from an organic compound with an ink-jet method, and forms a hole-injection layer, and the process which applies the ink constituent containing the luminescent material which consists of an organic compound with an ink-jet method, and forms a luminous layer.

[Claim 2] The manufacture method of the organic EL element according to claim 1 characterized by for the aforementioned organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this on a substrate, and forming the aforementioned hole-injection layer and the aforementioned luminous layer in the field between these septa.

[Claim 3] The manufacture method of the organic EL element according to claim 1 characterized by for the aforementioned organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this, and forming the aforementioned hole-injection layer and the aforementioned luminous layer through the consecutive-processing process of oxygen gas plasma and fluorocarbon gas plasma on a substrate.

[Claim 4] The manufacture method of the organic EL element according to claim 1 characterized by removing the solvent of this ink constituent after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound with an ink-jet method, removing the solvent of this ink constituent after applying the ink constituent containing obtaining a hole-injection layer and the luminescent material which consists of the aforementioned organic compound with an ink-jet method, and obtaining a luminous layer.

[Claim 6] The manufacture method of an organic EL element given in either according to claim 1 to 5 which is characterized by the contact angle to the material from which the viscosity of the ink constituent containing the aforementioned hole-injection material or the aforementioned

luminescent material constitutes 1 - 20 mPa-s, and surface tension constitutes the nozzle side of 20 - 70 mN/m and an ink-jet head being 30-170 degrees.

[Claim 7] The manufacture method of the organic EL element according to claim 6 characterized by the solid part concentration of the aforementioned ink constituent being 0.01 – 10.0wt%.

[Claim 8] The organic EL element according to claim 6 or 7 characterized by the vapor pressure of the aforementioned ink constituent containing a kind of solvent of 0.001 - 50mmHg (room temperature) at least.

[Claim 9] The manufacture method of the organic EL element according to claim 8 characterized by the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[Claim 10] The manufacture method of the organic EL element according to claim 6 to 9 characterized by the aforementioned ink constituent containing a glycol-ether system acetic acid.

[Claim 11] the aforementioned ink constituent — a lower alcohol — less than [20wt%] — the manufacture method of the organic EL element according to claim 6 to 10 characterized by containing

[Claim 12] The manufacture method of the organic EL element according to claim 6 characterized by the aforementioned ink constituent containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

[Claim 13] Furthermore, the manufacture method of the organic EL element according to claim 12 characterized by containing a silane coupling agent as a heat-curing agent.

[Claim 14] The manufacture method of the organic EL element according to claim 6 characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[Claim 15] The manufacture method of the organic EL element according to claim 14 characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

[Claim 16] The organic EL element manufactured by the method according to claim 1 to 15.

[Claim 17] The ink constituent characterized by being an ink constituent containing the hole-injection material or luminescent material applied by the ink-jet method in manufacture of an organic EL element, and the contact angle to the material from which viscosity constitutes 1 – 20 mPa-s, and surface tension constitutes the nozzle side of 20 – 70 mN/m and an ink-jet head being 30-170 degrees.

[Claim 18] The ink constituent according to claim 17 with which solid part concentration is characterized by ***** at 0.01 - 10.0wt%.

[Claim 19] The ink constituent according to claim 17 or 18 characterized by vapor pressure containing a kind of solvent of 0.001 - 50mmHg (room temperature) at least.

[Claim 20] They are the feature and an ink constituent according to claim 19 about the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[Claim 21] It is an ink constituent to the claim 17 characterized by including the aforementioned glycol-ether system acetic acid, or either of 20.

[Claim 22] a lower alcohol — less than [20wt%] — the ink constituent according to claim 17 to 21 characterized by containing

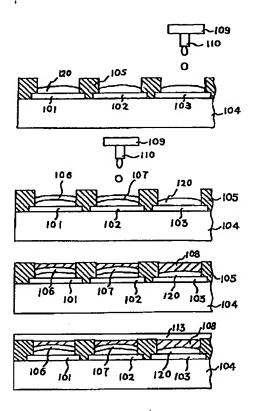
[Claim 23] The ink constituent according to claim 17 characterized by the aforementioned ink constituent containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

[Claim 24] Furthermore, the ink constituent according to claim 17 characterized by containing a silane coupling agent as a heat-curing agent.

[Claim 25] The ink constituent according to claim 17 characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[Claim 26] The ink constituent according to claim 25 characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

Drawing selection [R pr sentativ drawing]



Copyright (C); 2000 Japan Patent Office

				5-0
19				
	c	*		
	•			

JAPANESE [JP,2000-323276,A]	
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS	******
[Translation done.]	

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[The technical field to which invention belongs] It is related with the manufacture method of the organic EL element which is an electric light emitting device used for a display, the display light source, etc., an organic EL element, and the ink constituent used for the formation of a hole-injection layer or a luminous layer.

[0002]

[Description of the Prior Art] Development of the light emitting device which used the organic substance for the luminous layer as a spontaneous luminescence type display replaced with a liquid crystal display is accelerating in recent years. As a formation process of a luminous layer which consists of the organic substance in organic EL (electroluminescence) element, it is Appl.Phys.Lett.51(12) and 21. September How to form low-molecular material by the vacuum deposition as shown in 913 pages of 1987 Appl.Phys.Lett.71(1), 7 July The method of applying polymeric materials as shown from 34 pages of 1997 is mainly developed.

[0003] When using low-molecular system material as a means of colorization, the method of carrying out the vacuum evaporation of the luminescent material of the different luminescent color over the mask of a predetermined pattern to a desired pixel corresponding point, and forming it in it is performed. On the other hand, when using macromolecule system material, since patterning can be done minutely and easily, the colorization using the ink-jet method attracts attention. About production of the organic EL element by the ink-jet method, it is indicated by JP,7-235378,A, JP,10-12377,A, JP,10-153987,A, JP,11-40358,A, and JP,11-54270,A, for example.

[0004] Furthermore, by the organic EL element, in order to raise luminous efficiency and endurance, it is shown that a hole-injection layer or an electron hole transporting bed is formed between an anode plate and a luminous layer (Appl.Phys.Lett.51, 913 pages of 21 September 1987). Conventionally, a film is formed by the applying methods, such as a spin coat, using a conductive polymer, for example, the poly thiophene derivative, and the poly aniline derivative (357,477 Nature, 1992) as a buffer layer or a hole-injection layer. As the hole-injection layer or electron hole transporting bed of low-molecular system material, the phenylamine derivative was formed and used in many cases by vacuum evaporationo. [0005]

[Problem(s) to be Solved by the Invention] In the organic EL element, in case the laminated structure of a hole-injection layer and a luminous layer is formed, a means not to make material useless, but to carry out patterning of the organic thin film which constitutes a hole-injection layer and a luminous layer that it is simple and minutely, and to form membranes is demanded. [0006] The ink-jet method is very effective. However, manufacture of the ink constituent which can form membranes as a functional film, without filling the stable regurgitation nature by the ink-jet method, and spoiling the property of material is a very difficult technical problem. The ink

constituent is indicated by JP,11-40358,A and JP,11-54270,A in manufacture of an organic EL element. The constituent which used high-boiling point solvents, such as a glycerol and a diethylene glycol, as DMF (dimethylformamide) or a wetting agent is indicated by these publications from the point of regurgitation nature. DMF has a problem in the stability over heat, an acid, and alkali, and higher alcohol, such as a glycerol and a diethylene glycol, has the problem which reacts in process of a PPV precursor and conjugation, and checks a property, when using a poly para-phenylene vinylene (PPV) as a green luminescent material. Moreover, especially a glycerol is difficult to remove.

[0007] Moreover, if the diameter of a nozzle tends to be made small and it is going to form a smaller ink-jet drop, in order to raise the resolution of patterning, the more a drop will become small, the more ink has also produced the problem of becoming easy to get dry.

[0008] Furthermore, when carrying out the laminating of the organic layer not only by the ink-jet method but by the applying method, the so-called compatibility in which the solvent of a constituent dissolves the organic film of a ground layer poses a problem. It is the case where a luminous layer is specifically formed on a hole-injection layer (or electron hole transporting bed). [0009] Then, the place made into the technical problem of this invention is located in the place which provides the method row which manufactures the organic EL element which consists of an organic cascade screen which excelled [low cost / simplicity, a short time, and] in the property with the ink constituent which makes it possible. [0010]

[Means for Solving the Problem] According to this invention, the manufacture method of the organic EL element of following the (1) - (5) is offered.

[0011] (1) The manufacture method of the organic EL element characterized by to provide the process which applies the ink constituent containing the hole-injection material which is the manufacture method of the organic EL element of structure of having ****(ed) the hole-injection layer and the luminous layer by the anode plate and cathode, and becomes a predetermined field on a substrate from an organic compound with an ink-jet method, and forms a hole-injection layer, and the process which applies the ink constituent containing the luminescent material which consists of an organic compound with an ink-jet method, and forms a luminous layer.

[0012] By the method of starting which forms both the hole-injection layer which consists of an organic compound, and a luminous layer by the ink-jet method, the method concerned can form all organic layers by the simple method, and can make any layer a high performance.

[0013] In addition, in this invention, a hole-injection layer is a layer into which an electron hole may be made to inject effective in a luminous layer from an anode plate side, and it also has an electron hole transportation function. Moreover, you may prepare the electron hole transporting bed which has an electron hole transportation function with a hole-injection layer in another layer.

[0014] (2) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this on a substrate, and forming the aforementioned hole-injection layer and the aforementioned luminous layer in the field between these septa. [0015] A high definition organic EL element can be easily obtained with multiple color, without mixing a different luminous layer by the method concerned of (2).

[0016] (3) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this, and forming the aforementioned hole-injection layer and the aforementioned luminous layer through the consecutive-processing process of oxygen gas plasma and fluorocarbon gas plasma on a substrate.

[0017] By the method concerned of (3), the wettability difference in a drop can be given on a substrate, and detailed patterning of an ink-jet drop becomes possible.

[0018] (4) The manufacture method of the organic EL element of (1) characterized by removing the solvent of this ink constituent after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound with an ink-jet method, removing the solvent of this ink constituent after applying the ink constituent containing obtaining a hole-injection layer and the luminescent material which consists of the aforementioned organic compound with an ink-jet method, and obtaining a luminous layer.

[0019] The organic solid-state thin film as the desired hole-injection layer and desired luminous layer of a property can be formed by the method concerned of (4).

[0020] (5) The manufacture method of the organic EL element of (1) characterized by to make the material of this ink constituent harden or conjugate with heat treatment further, and to obtain a luminous layer after applying the ink constituent containing making the material of this ink constituent harden or conjugate with heat treatment further, and obtaining a hole-injection layer after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound by the ink-jet method, and the luminescent material which consists of the aforementioned organic compound with an ink-jet method.

[0021] The hole-injection layer and luminous layer which have the outstanding function by the method concerned of (5) can be formed.

[0022] Moreover, according to this invention, following (6) or the ink constituent of (15) is offered. (6) The ink constituent characterized by being an ink constituent containing the hole-injection material or luminescent material applied by the ink-jet method in manufacture of an organic EL element, and the contact angle to the material from which viscosity constitutes 1 – 20 mPa-s, and surface tension constitutes the nozzle side of 20 – 70 mN/m and an ink-jet head being 30–170 degrees.

[0023] the case where it applies especially by the ink-jet method according to the ink constituent concerned of (6) -- a nozzle -- while pressing down the blinding of a hole, and the flight deflection of an ink drop, the regurgitation is made smooth, and it becomes controllable [discharge quantity and regurgitation timing], and the stable regurgitation by the ink-jet method becomes possible

[0024] (7) (6) ink constituents with which solid part concentration is characterized by ***** at 0.01 - 10.0wt%.

[0025] According to the ink constituent concerned of (7), when applying by the ink-jet method, it becomes possible to obtain desired thickness, without spoiling regurgitation nature.

[0026] (8) (6) or (7) ink constituents which are characterized by vapor pressure containing a kind of solvent of 0.001 - 50mmHg (room temperature) at least.

[0027] the time of applying by the ink jet according to the ink constituent concerned of (8) -- dryness of ink -- it can stop -- a nozzle -- the blinding in a hole can be lost

(9) It is the ink constituent of the feature and either of (8) about the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[0028] In case the ink constituent concerned of (9) distributes or dissolves stably and is applied by the ink-jet method, without spoiling the property of hole-injection material or luminescent material, the stable regurgitation of it becomes possible.

[0029] (10) The ink constituent of either (6) characterized by including a glycol-ether system acetic acid, or (9).

[0030] It not only can suppress dryness of ink, but according to the ink constituent concerned of (10), it can improve membrane formation nature.

[0031] (11) a lower alcohol -- less than [20wt%] -- the ink constituent of either (6) characterized by containing, or (10)

[0032] According to the ink constituent concerned of (11), in case it applies especially by the ink-jet method, it becomes possible to adjust surface tension and viscosity to a desired value, without spoiling the regurgitation nature of ink.

[0033] (12) The ink constituent of (6) characterized by the aforementioned ink constituent

2003/11/26 14:06

containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

[0034] According to the ink constituent concerned of (12), in case it applies especially by the ink-jet method, regurgitation nature and membrane formation nature are excellent, and it becomes possible to obtain a highly efficient hole-injection layer in an organic EL element. [0035] (13) The ink constituent of (12) characterized by furthermore containing a silane coupling agent as a heat-curing agent.

[0036] If the ink constituent concerned of (13) is used, the hole-injection layer which does not cause compatibility with a luminous layer in an organic EL element by applying especially by the ink-jet method can be formed.

[0037] (14) The ink constituent of (6) characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[0038] According to the ink constituent concerned of (14), it can consider as the green which was excellent in the regurgitation nature at the time of applying especially to the ink-jet method, and membrane formation nature, and was excellent in the luminescence property in the organic EL element, or the ink constituent for red luminous layers.

[0039] (15) The ink constituent of (14) characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

[0040] According to the ink constituent concerned of (15), it can consider as the green which was excellent in the regurgitation nature at the time of applying especially to the ink-jet method, membrane formation nature, and the luminescence property, or the ink constituent for red luminous layers.

[0041] The above (6) or the ink constituent of (15) can be suitably used in the formation process of a hole-injection layer or a luminous layer in the manufacture method of the organic EL element of (1) or (5), respectively.

[0042] Moreover, according to this invention, the highly efficient organic EL element obtained by the above-mentioned method is offered.

[0043]

[Embodiments of the Invention] Hereafter, the operation gestalt of this invention is explained in detail.

[0044] It is the method of applying on the substrate which the ink constituent which made the solvent dissolve or distribute the hole-injection material which serves as the manufacture method of the organic EL element by the ink-jet method of this invention from the organic substance which forms an element, and the luminescent material which becomes a row from the organic substance is made to breathe out from an ink-jet head, for example, a transparent electrode is formed, and constitutes a pixel, and forming a luminous layer in a hole-injection layer row. According to this ink-jet method, detailed patterning can be performed simple in a short time, and multiple-color-izing is possible. Moreover, material is not made useless, even if it becomes the substrate of a large area, since what is necessary is just to apply the material of an initial complement to a required place.

[0045] The structure of the head for ink jets used for the organic EL element of this invention in the manufacture method is shown in <u>drawing 1</u> and <u>drawing 2</u>. The head 10 for ink jets concerned is equipped with the nozzle plate 11 and diaphragm 13 made from stainless steel, and both are joined through the batch member (reservoir plate) 15. between a nozzle plate 11 and diaphragms 13 -- a batch -- two or more ink rooms 19 and ****** 21 are formed of the member 15 The ink room 19 and the interior of ****** 21 are filled with the ink constituent of this invention, and the ink room 19 and ****** 21 are opening them for free passage through a feed hopper 23. furthermore, the nozzle for injecting an ink constituent from the ink room 19 in the shape of JIETO to a nozzle plate 11 -- the hole 25 is formed the ink introduction for on the other hand supplying an ink constituent to the head 10 for ink jets at ****** 21 -- the hole 27

is formed Moreover, on the field which counters the ink room 19 of a diaphragm 13, and the field of an opposite side, it is made to correspond to the position of the aforementioned space 19, and the piezoelectric device 29 is joined.

[0046] This piezoelectric device 29 is located between the electrodes 31 of a couple, and if it energizes, it will bend so that a piezoelectric device 29 may project outside. The capacity of the ink room 19 increases by this. Therefore, the ink constituent equivalent to a part for the capacity which increased in the ink room 19 flows through a feed hopper 23 from ****** 21. Next, if the energization to a piezoelectric device 29 is canceled, both this piezoelectric device 29 and the diaphragm 13 will return to the original configuration. since space 19 also returns to the original capacity by this — the pressure of the ink constituent of the ink room 19 interior — going up — a nozzle — an ink constituent spouts towards a substrate from a hole 25 [0047] in addition, a nozzle — the periphery of a hole 25 — the flight deflection of an ink constituent, and a hole — in order to prevent plugging, the ** ink layer 26 is formed namely, a nozzle — the ** ink layer 26 which consists of a nickel-tetrafluoroethylene eutectoid deposit as the periphery of a hole 25 is shown in drawing 2 is formed

[0048] In the manufacture method of the organic EL element of this invention, the ink constituent containing the hole-injection material which is made to breathe out from the aforementioned head for ink jets, and is used, or luminescent material has the following properties.

[0049] The viscosity of an ink constituent is 1 - 20 mPa-s preferably, and is 2 - 8 mPa-s especially preferably. When the viscosity of an ink constituent is less than 1 mPa-s, solid part concentration becomes [too little] and control of discharge quantity not only becomes difficult, but may be unable to form enough films. the case where 20 mPa-s is exceeded --- a nozzle --- a possibility that an ink constituent cannot be made to breathe out smoothly from a hole -- it is -- a nozzle -- it may be necessary to change the specification of equipment, such as enlarging a hole case [furthermore,] viscosity is large -- a part for solid [in an ink constituent] -depositing -- easy -- a nozzle -- the blinding frequency of a hole becomes high [0050] Moreover, the surface tension of an ink constituent is 20 - 70 mN/m preferably, and is 25 - 45 mN/m especially preferably. By making it the surface tension of this range, the flight deflection in the case of the ink regurgitation can be stopped, the time of carrying out the regurgitation of the ink constituent, since the wettability on the nozzle side of an ink constituent will increase, if surface tension is less than 20 mN/m -- an ink constituent -- a nozzle -- it may adhere to the circumference of a hole asymmetrically in this case, a nozzle -- in order that attraction may work between the affixes made into the constituent adhering to the hole, and how to breathe out, the so-called flight deflection which will be breathed out by the uneven force and cannot reach a target position arises, and an ink constituent is natural -- the frequency also becomes high Moreover, since the configuration of the meniscus in the nose of cam of a nozzle will not be stabilized if 70 mN/m is exceeded, control of the discharge quantity of an ink constituent and regurgitation timing becomes difficult.

[0051] The contact angle to the material which constitutes the nozzle side which carries out the regurgitation of the ink constituent prepared in the head for ink jets is 30 degrees – 170 degrees preferably, and is 35 degrees – 65 degrees especially preferably. When an ink constituent has the contact angle of this range, the flight deflection of an ink constituent can be controlled and precise patterning becomes possible. Since the wettability to the material which constitutes the nozzle side of an ink constituent increases when this contact angle is less than 30 degrees, flight deflection arises like the case where it is surface tension, moreover, if it exceeds 170 degrees — an ink constituent and a nozzle — the interaction of a hole serves as the minimum, and since the configuration of the meniscus in the nose of cam of a nozzle is not stabilized, control of the discharge quantity of an ink constituent and regurgitation timing becomes difficult

[0052] Flight deflection means that the position which the dot reached produces a gap of 50

2003/11/26 14:06

micrometers or more to a target position here, when an ink constituent is made to breathe out from the aforementioned nozzle. mainly — a nozzle — it generates by the case where the wettability of a hole is uneven, the blinding by adhesion of the solid component of an ink constituent, etc.

[0053] 0.01 - 10.0wt% of the solid part concentration of an ink constituent is desirable to the whole constituent, and is still more desirable. [0.1 - 5.0wt% of] If solid part concentration is too low, in order to obtain required thickness, the number of times of the regurgitation will increase and mass-production efficiency will become bad. Moreover, even if too high, viscosity becomes high and regurgitation nature is affected.

[0054] As for a part for the above-mentioned solid one, it is desirable for the vapor pressure in a room temperature to dissolve or distribute to at least one or more solvents of 0.005 – 50mmHg. using the solvent it is hard to become it dry — an ink constituent — a nozzle — it can dry with a hole and can prevent adhesion for thickening, condensation, and solid taking place However, in membrane formation process, since removal of a solvent is difficult, a solvent with which vapor pressure is less than 0.005mmHg(s) is not suitable.

[0055] As such a solvent, glycol-ether system acetic acids, such as non-proton nature annular polar solvents, such as gamma-butyrolactone, N-methyl pyrrolidone (NMP), 1, and 3-dimethyl-2-imidazolidinone (DMI) and its derivative, or carbitol acetate (CA), and butyl carbitol acetate (BCA), are mentioned. Solvents, such as CA and BCA, are effective also at the point of raising membrane formation nature.

[0056] On the other hand, although lower alcohols, such as a methanol (MeOH), ethanol (EtOH), and propyl alcohol, are effective in manufacture of surface tension and viscosity, since volatility is high, it is desirable that it is less than [20wt%].

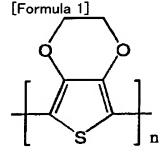
[0057] In addition, the above-mentioned property is suitable also as a property of the electron hole transportation material which constitutes this layer in the case of forming an electron hole transporting bed in an organic EL element.

[0058] Hereafter, this invention is explained still in detail in accordance with an example.

[0059] (Example 1) An example 1 is related with the ink constituent for hole-injection stratification applied by the ink-jet method in manufacture of an organic EL element.

[0060] PEDT which is the poly thiophene derivative as a hole-injection material in this invention (polyethylene dioxythiophene)

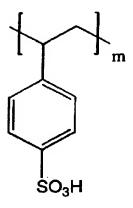
[0061]



[0062] PSS (polystyrene sulfonic acid)

[0063]

[Formula 2]



[0064] ******* was used. These can be purchased from a Beyer company as BAITORONP. As a hole-injection material (or electron hole transportation material used as the material of an electron hole transporting bed), although the poly aniline, a porphyrin compound, a pyridine derivative, etc. are mentioned, it is the macromolecule which is thermally durable and BAITORON P which can be distributed to polar solvents, such as water, is suitable for the ink-jet method. The ink constituent shown in Table 1 using BAITORON P was prepared. [0065]

[Table 1]

組成物	材料名	含有量 (wt%)
正孔注入/輸送材料	PEDT/PSS(パイトロンP)(水分散液)	7.25
	*	52.75
極性溶媒	メタノール	5
	イソプロピルアルコール	5
	1、3ージメチルー2ーイミダゾリジノン	30
シランカップリング剤	ァーグリンジルオキシブロビルトリメトキシシラン	0.08

[0066] In order to prevent compatibility with a luminous layer, the said weight addition was carried out with the conductive polymer, using gamma-glycidyloxypropyl trimethoxysilane as a silane coupling agent which constructs a bridge by heat-treatment. The solid part concentration of a final ink constituent was 0.16wt(s)%.

[0067] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink regurgitation nozzle side of the head for ink jets, regurgitation nature, patterning nature, and membrane formation nature is shown in Table 2. The following methods estimated the physical property and regurgitation property of an ink constituent.

[0068] Viscosity: The value in 20 degrees C was measured with E type viscometer.

[0069] Surface tension: Similarly the value in 20 degrees C was measured by the plate method.

[0070] Contact angle: It measured as a static contact angle on the material

(nickel-tetrafluoroethylene eutectoid plating hydrophobic layer) which constitutes the ink regurgitation nozzle side of the head for ink jets.

[0071] Regurgitation property: The head for ink jet printers (Epson MJ-930C) was used. Flight deflection measured impact dispersion of the ink drop on the substrate when setting distance of a head and a substrate to 0.6mm. a nozzle — a part for solid [of the ink constituent which carried out the continuation regurgitation (frequency of 7200Hz) of the ink constituent, and deposited as blinding frequency of a hole] etc. — a nozzle — the hole carried out blinding and the time taken to result in the state where it became regurgitation impotentia was measured [0072] Patterning nature, membrane—formation nature: After breathing out to the test cell shown in drawing 3 (a) and (b) and removing a solvent in a room temperature and a vacuum, 200 degrees C (condensation, flat nature, etc.) of membraneous qualities of the film which heat—treated for 10 minut s and was formed were observed under the microscope among the atmosphere. A test cell has the pixel (40-micrometer pitch) which carried out opening of the

2-micrometer thick polyimide 40 formed on the ITO substrate 41 with the diameter of 30 micrometer. Performing consecutive processing of oxygen gas plasma and fluorocarbon gas plasma before the regurgitation, the polyimide front face used what hydrophilicity-ized ***** and the ITO front face. In addition, the aforementioned plasma treatment may be which atmosphere in a vacuum and the atmosphere. And the ink constituent 44 was breathed out from the ink-jet head 43 of ink-jet equipment 42 to opening, and the film was obtained and evaluated. A result is shown in the following table 2.

[0073] [Table 2]

粘度 [mPa·s]	7.08
表面强力 [mN/m]	44.9
接触角[*]	66
目結束り顧度 [seo]	>10000
飛行ばらつき [µm]	±20
パターニング性	0
成膜性	Ø

[0074] As shown in Table 2, it was that to which regurgitation nature, patterning nature, and membrane formation nature reach sufficiency and practical use level. In addition, the place during composition of Table 1 (for example, the place which prepared the methanol (MeOH) and the constituent with which the addition of isopropyl alcohol (IPA) exceeds 20%, formed like the above, and was evaluated), or the place which prepared the constituent which did not add 1 and 3-dimethyl-2-imidazolidine (DMI), but was replaced with water, formed like the above, and was evaluated — the above — even if it fulfills a physical value, blinding has been started among the regurgitation by the thirst of an ink constituent

[0075] (Example 2) An example 2 is related with the ink constituent for luminous layers. [0076] In this invention, poly (PARAFENIREMBINIREN) (PPV) was used as a green luminescent material.

[0077] as an organic compound which can form a luminous layer, the poly propine vinylenes, such as the poly alkyl thiophenes, such as PTV (poly (2, 5-thienylene vinylene)), PFV (poly (2, 5-FURIREN vinylene)), poly para-phenylene, and the poly alkyl fluorene, a pyrazoline dimer, a kino lysine carboxylic acid, benzo pyrylium perchlorate, a benzo PIRANO kino lysine, a phenanthroline europium complex, etc. mention other than PPV -- having -- these -- one sort -- or two or more sorts can be mixed and it What consists of a macromolecule organic compound also in these is desirable. A macromolecule organic compound is excellent in membrane formation nature, and the endurance of a luminous layer is very good. Macromolecule system material has molecular design tuck length latus flexibility, and the rational design of EL light emitting device is possible for it. Moreover, it has the band gap of a visible region, and comparatively high conductivity, and a conjugated-system macromolecule has such a remarkable inclination especially. As a luminous layer material, the precursor of the conjugated-system macromolecule which conjugates by the conjugated-system macromolecule itself or heating (membrane formation) is used. PPV or especially its derivative is desirable also in these. As a precursor of a PPV derivative, a MO-PPV (poly (2, 5-dimethoxy -1, 4-phenylenevinylene)) precursor, a CN-PPV (poly (2, 5-screw hexyloxy-1, 4-phenylene -(1-cyano vinylene))) precursor, etc. are mentioned. The precursor before conjugation (membrane formation) of PPV or its derivative is meltable to water or a polar solvent, and fits the pattern formation by the ink-jet method. Furthermore, PPV or its derivative has strong fluorescence, and since it is also the conductive polymer which the pi electron of a double bond has delocalized on a polymer chain, the thin film of PPV can function also as a hole-injection transporting bed, and can obtain a highly efficient organic EL element. [0078]

[Formula 3]

[0079] The ink constituent shown in Table 3 using the poly (PARAFENIREMBINIREN) precursor (water / MeOH=5/95 mixed solution) was prepared. Solid part concentration was 0.3wt(s)%. [0080]

[Table 3]

組成物	材料名	含有量 (wt%)
発光材料	PPV前驱体溶液 (1.5wt%)	20
	(水/メタノール=5/95 混合溶液)	
種性溶媒	1、3ージメテルー2ーイミダゾリジノン	70
	ブチルカルビト―ルアセテート	10

[0081] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink regurgitation nozzle side of the head for ink jets, regurgitation nature, patterning nature, and membrane formation nature is shown in Table 4. The same method as an example 1 estimated the physical property and regurgitation property of an ink constituent. After the regurgitation, in the room temperature and the vacuum, membrane formation nature removed the solvent, among nitrogen-gas-atmosphere mind, 150 degrees C, is what was processed for 4 hours, and evaluated it.

[0082]

[Table 4]

乾度 [mPa·s]	3.21
表面張力 [mN/m]	37.6
接触角[]	56.6
目詰まり類度 [sec]	>10000
飛行ばらつき [μm]	±25
パターニング性	•
成膜性	•

[0083] As shown in Table 4, it was that to which regurgitation nature, patterning nature, and membrane formation nature reach sufficiency and practical use level. On the other hand, although it was satisfactory to regurgitation nature for example, when the ink constituent which replaced butyl carbitol acetate (BCA) with the glycerol was prepared and the same membrane formation and same evaluation as the above were performed or it replaced DMI by the dimethylformamide (DMF), luminous efficiency was low and also shifted the luminescent color to the short wavelength side. the case where he wants to make solid part concentration deeper than 0.3wt(s)% — a precursor solution — more than 20wt% — if it adds — a MeOH content — increasing — ink — becoming it dry — being easy — since flight deflection and blinding were produced, what ****(ed) and condensed the precursor solution was used [0084] (Example 3) An example 3 is related with the ink constituent for luminous layers. [0085] In this example, what added the rhodamine 101 which is a low—molecular fluorochrome as a red luminescent material was used for the PPV precursor ink constituent used in the example 2.

[0086] The method of doping the fluorochrome of a low-molecular system can change the luminescence property of a luminous layer, for example, is very effective considering the improvement in luminous efficiency, or luminescence wavelength as a frog means. The high red of color purity and green luminescence can be obtained by the dope of a fluorochrome.

[0087] As a fluorochrome used for a red luminous layer, DCM of laser coloring matter, a rhodamine or a rhodamine derivative, a perylene, etc. can be used. Since it is low-molecular, it is

meltable to a solvent, and these fluorochromes have PPV etc. and good compatibility and formation of the uniform and stabilized luminous layer is easy for them. As a rhodamine derivative fluorochrome, Rhodamine B, the Rhodamine B base, rhodamine 6G, rhodamine 101 perchlorate, etc. are mentioned, for example, and two or more sorts of these may be mixed. [0088] Moreover, as a fluorochrome used for a green luminous layer, a Quinacridone, rubrene, DCJT(s), and those derivatives are mentioned. Like the above-mentioned red fluorochrome, since these fluorochromes are low-molecular, PPV etc. and compatibility are good meltable and formation of a luminous layer is easy for them to a solvent.

[0089] In this example, the ink constituent for red luminous layers shown in the following table 5 was prepared.

[0090]

[Table 5]

組成物	材料名	含有量 (wt%)
発光材料	PPV醇堅体溶液 (1.5wt%)	20
	(水/メタノール=5/95 混合溶液)	
	ローダミン101	0.0045
		前駆体固型分比
		1.5wt%
極性溶媒	1、3ージメチルー2ーイミダゾリジノン	70
	ブチルカルビトールアセテート	10

[0091] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink regurgitation nozzle side of the head for ink jets, regurgitation nature, patterning nature, and membrane formation nature is shown in Table 6. The same method as an example 2 estimated the physical property of an ink constituent and a regurgitation property, and membrane formation nature.

[0092] [Table 6]

[, dbio o]	
粘度 [mPa·s]	3.27
表面張力 [mN/m]	37.4
接触角["]	60
目詰まり類度 [sec]	>10000
飛行ばらつき [μm]	±25
パターニング性	0
成蹊性	0

[0093] As shown in Table 6, it was that to which regurgitation nature, patterning nature, and membrane formation nature reach sufficiency and practical use level. the amount of dopes of a rhodamine 101 — a PPV precursor — receiving — 1.5wt(s)% — when it added, it was the most efficient and red luminescence was shown

[0094] (Example 4) An example 4 is related with the manufacture method of the organic EL element by the ink-jet method. <u>Drawing 4</u> shows the manufacturing process of the full color organic EL element of three colors.

[0095] While the transparent substrate 104 is a base material, it functions as a field which takes out light. Therefore, the transparent substrate 104 is chosen in consideration of the transparency property and thermal stability of light. As a transparent substrate material, although a glass substrate, transparent plastics, etc. are mentioned, for example, since it excels in thermal resistance, a glass substrate is desirable.

[0096] First, the pixel electrodes 101, 102, and 103 were formed on the transparent substrate 104. As the formation method, although photo lithography, vacuum deposition, the sputtering method, the metal—fog method, etc. are mentioned, for example, being based on photo lithography is desirable. As a pixel electrode, a transparent pixel electrode is desirable, and a tin-oxide film, an ITO film, the multiple-oxide film of indium oxide and a zinc oxide, etc. are mentioned as a material which constitutes a transparent pixel electrode.

[0097] Next, the septum (bank) 105 was formed by the photosensitive polyimide, and it buried each above transparent pixel inter-electrode. Thereby, improvement in contrast, prevention of the color mixture of luminescent material, the optical leak from between a pixel and pixels, etc. can be prevented.

[0098] although it obtains, and it will not be limited especially if it is, organic materials, such as acrylic resin, an epoxy resin, and a photosensitive polyimide, are desirable, for example from the thing which have endurance to the solvent of EL material as a material which constitutes a septum 105 and for which—izing can be carried out [Teflon] by fluorocarbon gas plasma treatment You may be the laminating septum which made inorganic material, such as liquefied glass, the lower layer. Moreover, a septum 105 mixes carbon black etc. in the above—mentioned material, and is good also as a black resist. As the formation method of this septum 105, photo lithography etc. is mentioned, for example.

[0099] Just before applying the ink constituent for hole-injection layers (further electron hole transporting bed), continuation plasma treatment of the oxygen gas of the above-mentioned substrate and fluorocarbon gas plasma was performed. Thereby, ***** and an ITO front face are hydrophilicity-ized and a polyimide front face can perform wettability control by the side of the substrate for carrying out patterning of the ink-jet drop minutely. As equipment which generates plasma, it can use similarly with the equipment which generates plasma in a vacuum, or the equipment which generates plasma in the atmosphere.

[0100] Next, the ink constituent for hole-injection layers mentioned in the example 1 was breathed out from the head 110 (Epson MJ-930C) of ink-jet print equipment 109, and the patterning application was performed on each pixel electrodes 101 and 102 and 103. The solvent was removed on a room temperature and the conditions of 20 minutes after an application and among the vacuum (1torr), and the ink constituent for luminous layers mentioned in the examples 2 and 3 and the hole-injection layer 120 not dissolving were formed among the atmosphere after that with 200 degrees C (on a hot plate), and heat treatment for 10 minutes. Thickness was 40nm. Although each pixel formed the common hole-injection layer in this example, depending on the case, you may form using the hole-injection material (or electron hole transportation material) which was suitable for the luminous layer the whole luminous layer.

[0101] The ink constituent for red luminous layers furthermore mentioned in the example 3 and the ink constituent for green luminous layers mentioned to the row in the example 2 were applied to the pixel electrode 101 row in the shape of PATANIN on 102 through the hole-injection layer 120 top with the ink-jet method. After an application and among the vacuum (1torr), the solvent was made to remove and conjugate continuously with 150 degrees C and heat treatment of 4 hours among nitrogen-gas-atmosphere mind on a room temperature and the conditions of 20 minutes, and the red luminous layer 106 and the green luminous layer 107 were formed. Thickness was 50nm. The luminous layer conjugated with heat treatment is insoluble to a solvent.

[0102] According to this ink-jet method, detailed patterning can be performed simple in a short time. Moreover, it is possible by changing the solid part concentration and discharge quantity of an ink constituent to change thickness.

[0103] Moreover, before forming a luminous layer, you may perform continuation plasma treatment of oxygen gas and fluorocarbon gas plasma in the hole-injection layer 120. A fluorine ghost layer is formed on a hole injection or the electron hole transporting bed 120 by this, and ionization potential can offer the incr ase of hole-injection efficiency, and the organic high EL element of luminous efficiency by the bird clapper highly.

[0104] Subsequently, the blue luminous layer 108 was formed on the pixel electrode 103 through the red luminous layer 106, green luminous layer 107, and hole-injection layer 120 top. Thereby, it not only forms the three primary colors of red, green, and blue, but it can bury and carry out flattening of the level difference of a red luminous layer and the 106 green luminous layer 107,

and a septum 105. Thereby, vertical inter-electrode short-circuit can be prevented certainly. By adjusting the thickness of a blue luminous layer, in a laminated structure with a red luminous layer and a green luminous layer, a blue luminous layer acts as an electron-injection transporting bed, and does not emit light blue.

[0105] It is not limited especially as the formation method of this blue luminous layer 108, but membranes can be formed also by the general spin coat method as a wet method, or the ink-jet method. In this example, the spin coat of the xylene solution of the poly dioctyl fluorene was carried out, and the blue luminous layer 108 of 45nm of thickness was formed.

[0106] The poly dihexyl fluorene which is otherwise the poly fluorene derivative as a blue luminous layer, and a copolymer with other polymerization machines are mentioned, and an organic compound with a blue fluorochrome or electron-injection transportation ability may be added.

[0107] As an organic compound which can form an electron-injection transporting bed, PBD, the OKISA diazole derivative of OXD-8 grade, DSA, an aluminum quinol complex, Bebq, a triazole derivative, an azomethine complex, a porphin complex, etc. are mentioned. [0108] Since a full color organic EL element can be formed by combining with other organic luminescent material used for an ink-jet method even if it is the luminescent material which is seldom suitable for an ink-jet method by forming two colors with an ink-jet method among organic luminous layers, and forming other Isshiki by the conventional method of application like this example, the flexibility of an element design increases. As the conventional methods of application other than an ink-jet method, print processes, a replica method, a dipping method, the spin coat method, the cast method, the capillary-tube method, the roll coat method, the bar coat method, etc. are mentioned.

[0109] Finally, cathode (counterelectrode) 113 was formed. As cathode 113, a metal thin film electrode is desirable, and Mg, Ag, aluminum, Li, etc. are mentioned as a metal which constitutes cathode, for example. Moreover, the alloy which can use a small material of a work function other than these, for example, contains alkali metal, alkaline earth metal, such as calcium, and these can be used. Moreover, a metaled fluoridation object can also be adapted. Such cathode 113 can be formed by the vacuum deposition, the spatter, etc. In this example, calcium was carried out by the vacuum heating vacuum deposition, 1200nm laminating of the 100nm of the aluminum was further carried out by the spatter, and it considered as cathode.

[0110] Furthermore, you may form a protective coat on cathode 113. By forming a protective coat, cathode 113 and degradation of each luminous layers 106, 107, and 108, an injury, ablation, etc. were able to be prevented.

[0111] As a component of such a protective coat, an epoxy resin, acrylic resin, liquefied glass, etc. are mentioned. Moreover, as the formation method of a protective coat, the spin coat method, the casting method, a dipping method, the bar coat method, the roll coat method, the capillary—tube method, etc. are mentioned, for example.

[0112] In the organic EL element obtained by this example, two or more 100 cd/m brightness was obtained [the low battery not more than 5V] for the pixel of each color. Moreover, in the red pixel and green pixel which were formed with the ink-jet method, luminous efficiency was 0.15 lm/W and 0.25 lm/W, respectively, and the luminescence life (time when continuation luminescence is carried out, until it impresses fixed current, and it falls 50% to initial brightness) was also 2000 hours or more.

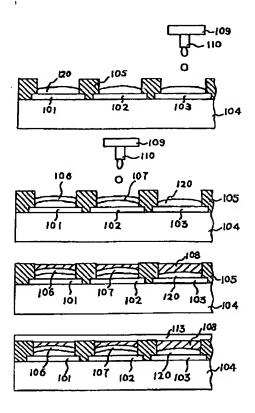
[0113] It was of the same grade as the thing of the red light emitting device which formed the hole-injection layer and the luminous layer by the same laminated structure on the spin coat using the same material as the above, and a green light emitting device. Thus, the property which was excellent also in the ink-jet method was able to be shown, and the element which is not inferior to a spin coat article was able to be formed.

[0114]

[Effect of the Invention] Above, according to this invention, both a hole-injection layer and a

luminous layer can be formed by the ink-jet method, and an organic EL element can be obtained simply quickly by the low cost. Moreover, the ink constituent for hole injections and the ink constituent for luminescence material layers excellent in regurgitation nature, patterning nature, and membrane formation nature were able to be offered. Moreover, using this ink constituent, the pattern formation of a hole injection or an electron hole transporting bed, and the luminous layer can be carried out simple and easily with an ink-jet method, and the highly minute full color organic EL element which was excellent in the property which consists of a laminated structure can be manufactured.

Drawing selection [Repr sentativ drawing]



Copyright (C); 2000 Japan Patent Office

JARANESE [JP,2000-323276,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

* NOTICES *

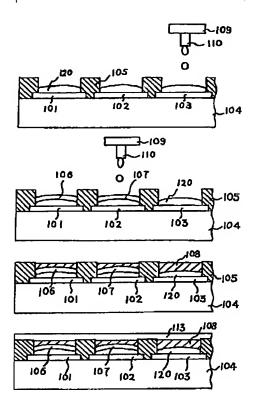
Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL FIELD

[The technical field to which invention belongs] It is related with the manufacture method of the organic EL element which is an electric light emitting device used for a display, the display light source, etc., an organic EL element, and the ink constituent used for the formation of a hole-injection layer or a luminous layer.

Drawing selection [Representative drawing]



Copyright (C); 2000 Japan Patent Office

<u>JAPANESE</u> [JP,2000-323276,A]
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS
[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

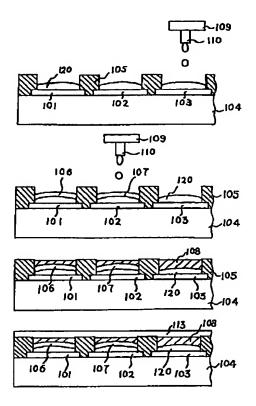
PRIOR ART

[Description of the Prior Art] Development of the light emitting device which used the organic substance for the luminous layer as a spontaneous luminescence type display replaced with a liquid crystal display is accelerating in recent years. As a formation process of a luminous layer which consists of the organic substance in organic EL (electroluminescence) element, it is Appl.Phys.Lett.51(12) and 21. September How to form low-molecular material by the vacuum deposition as shown in 913 pages of 1987 Appl.Phys.Lett.71(1), 7 July The method of applying polymeric materials as shown from 34 pages of 1997 is mainly developed.

[0003] When using low-molecular system material as a means of colorization, the method of carrying out the vacuum evaporation of the luminescent material of the different luminescent color over the mask of a predetermined pattern to a desired pixel corresponding point, and forming it in it is performed. On the other hand, when using macromolecule system material, since patterning can be done minutely and easily, the colorization using the ink-jet method attracts attention. About production of the organic EL element by the ink-jet method, it is indicated by JP,7-235378,A, JP,10-12377,A, JP,10-153987,A, JP,11-40358,A, and JP,11-54270,A, for example.

[0004] Furthermore, by the organic EL element, in order to raise luminous efficiency and endurance, it is shown that a hole-injection layer or an electron hole transporting bed is formed between an anode plate and a luminous layer (Appl.Phys.Lett.51, 913 pages of 21 September 1987). Conventionally, a film is formed by the applying methods, such as a spin coat, using a conductive polymer, for example, the poly thiophene derivative, and the poly aniline derivative (357,477 Nature, 1992) as a buffer layer or a hole-injection layer. As the hole-injection layer or electron hole transporting bed of low-molecular system material, the phenylamine derivative was formed and used in many cases by vacuum evaporationo.

Drawing selection [R presentative drawing]



Copyright (C); 2000 Japan Patent Office

JAPANESE [JP,2000-323276,A]	
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS	
[Translation done.]	

* NOTICES *

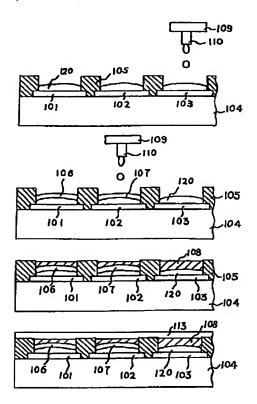
Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] Above, according to this invention, both a hole-injection layer and a luminous layer can be formed by the ink-jet method, and an organic EL element can be obtained simply quickly by the low cost. Moreover, the ink constituent for hole injections and the ink constituent for luminescence material layers excellent in ******, patterning nature, and membrane formation nature were able to be offered. Moreover, using this ink constituent, the pattern formation of a hole injection or an electron hole transporting bed, and the luminous layer can be carried out simple and easily with an ink-jet method, and the highly minute full color organic EL element which was excellent in the property which consists of a laminated structure can be manufactured.

Drawing selection [Representative drawing]



Copyright (C); 2000 Japan Patent Office

JAPANESE [JP,2000-323276,A]
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS
[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2,**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL PROBLEM

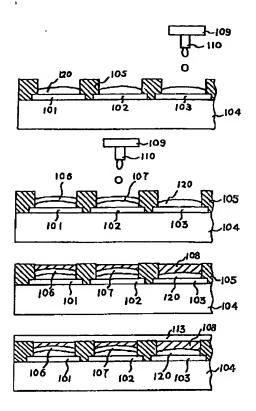
[Problem(s) to be Solved by the Invention] In the organic EL element, in case the laminated structure of a hole-injection layer and a luminous layer is formed, a means not to make material useless, but to carry out patterning of the organic thin film which constitutes a hole-injection layer and a luminous layer that it is simple and minutely, and to form membranes is demanded. [0006] The ink-jet method is very effective. However, manufacture of the ink constituent which can form membranes as a functional film, without filling the stable regurgitation nature by the ink-jet method, and spoiling the property of material is a very difficult technical problem. The ink constituent is indicated by JP,11-40358,A and JP,11-54270,A in manufacture of an organic EL element. The constituent which used high-boiling point solvents, such as a glycerol and a diethylene glycol, as DMF (dimethylformamide) or a wetting agent is indicated by these publications from the point of regurgitation nature. DMF has a problem in the stability over heat, an acid, and alkali, and higher alcohol, such as a glycerol and a diethylene glycol, has the problem which reacts in process of a PPV precursor and conjugation, and checks a property, when using a poly para-phenylene vinylene (PPV) as a green luminescent material. Moreover, especially a glycerol is difficult to remove.

[0007] Moreover, if the diameter of a nozzle tends to be made small and it is going to form a smaller ink-jet drop, in order to raise the resolution of patterning, the more a drop will become small, the more ink has also produced the problem of becoming easy to get dry.

[0008] Furthermore, when carrying out the laminating of the organic layer not only by the ink-jet method but by the applying method, the so-called compatibility in which the solvent of a constituent dissolves the organic film of a ground layer poses a problem. It is the case where a luminous layer is specifically formed on a hole-injection layer (or electron hole transporting bed).

[0009] Then, the place made into the technical problem of this invention is located in the place which provides the method row which manufactures the organic EL element which consists of an organic cascade screen which excelled [low cost / simplicity, a short time, and] in the property with the ink constituent which makes it possible.

Drawing selection [Repres ntative drawing]



Copyright (C); 2000 Japan Patent Office

JAPANESE [JP,2000-323276,A]	
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS	
[Translation done.]	

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] According to this invention, the manufacture method of the organic EL element of following the (1) - (5) is offered.

[0011] (1) The manufacture method of the organic EL element characterized by to provide the process which applies the ink constituent containing the hole-injection material which is the manufacture method of the organic EL element of structure of having ****(ed) the hole-injection layer and the luminous layer by the anode plate and cathode, and becomes a predetermined field on a substrate from an organic compound with an ink-jet method, and forms a hole-injection layer, and the process which applies the ink constituent containing the luminescent material which consists of an organic compound with an ink-jet method, and forms a luminous layer.

[0012] By the method of starting which forms both the hole-injection layer which consists of an organic compound, and a luminous layer by the ink-jet method, the method concerned can form all organic layers by the simple method, and can make any layer a high performance.

[0013] In addition, in this invention, a hole-injection layer is a layer into which an electron hole may be made to inject effective in a luminous layer from an anode plate side, and it also has an electron hole transportation function. Moreover, you may prepare the electron hole transporting bed which has an electron hole transportation function with a hole-injection layer in another layer.

[0014] (2) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this on a substrate, and forming the aforementioned hole-injection layer and the aforementioned luminous layer in the field between these septa. [0015] A high definition organic EL element can be easily obtained with multiple color, without mixing a different luminous layer by the method concerned of (2).

[0016] (3) The manufacture method of the organic EL element of (1) characterized by for an organic EL element being an element which has two or more pixels, preparing on a substrate the septum which separates every pixel of this, and forming the aforementioned hole-injection layer and the aforementioned luminous layer through the consecutive-processing process of oxygen gas plasma and fluorocarbon gas plasma on a substrate.

[0017] By the method concerned of (3), the wettability difference in a drop can be given on a substrate, and detailed patterning of an ink-jet drop becomes possible.

[0018] (4) The manufacture method of the organic EL element of (1) characterized by removing the solvent of this ink constituent after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound with an ink-jet method, removing the solvent of this ink constituent after applying the ink constituent containing obtaining a hole-injection layer and the luminescent material which consists of the aforementioned organic compound with an ink-jet method, and obtaining a luminous layer.

[0019] The organic solid-state thin film as the desired hole-injection layer and desired luminous

layer of a property can be formed by the method concerned of (4).

[0020] (5) The manufacture method of the organic EL element of (1) characterized by to make the material of this ink constituent harden or conjugate with heat treatment further, and to obtain a luminous layer after applying the ink constituent containing making the material of this ink constituent harden or conjugate with heat treatment further, and obtaining a hole-injection layer after applying the ink constituent containing the hole-injection material which consists of the aforementioned organic compound by the ink-jet method, and the luminescent material which consists of the aforementioned organic compound with an ink-jet method.

[0021] The hole-injection layer and luminous layer which have the outstanding function by the method concerned of (5) can be formed.

[0022] Moreover, according to this invention, following (6) or the ink constituent of (15) is offered. (6) The ink constituent characterized by being an ink constituent containing the hole-injection material or luminescent material applied by the ink-jet method in manufacture of an organic EL element, and the contact angle to the material from which viscosity constitutes 1 – 20 mPa-s, and surface tension constitutes the nozzle side of 20 – 70 mN/m and an ink-jet head being 30–170 degrees.

[0023] the case where it applies especially by the ink-jet method according to the ink constituent concerned of (6) — a nozzle — while pressing down the blinding of a hole, and the flight deflection of an ink drop, the regurgitation is made smooth, and it becomes controllable [discharge quantity and regurgitation timing], and the stable regurgitation by the ink-jet method becomes possible

[0024] (7) (6) ink constituents with which solid part concentration is characterized by ***** at 0.01 - 10.0wt%.

[0025] According to the ink constituent concerned of (7), when applying by the ink-jet method, it becomes possible to obtain desired thickness, without spoiling regurgitation nature.

[0026] (8) (6) or (7) ink constituents which are characterized by vapor pressure containing a kind of solvent of 0.001 - 50mmHg (room temperature) at least.

[0027] the time of applying by the ink jet according to the ink constituent concerned of (8) -- dryness of ink -- it can stop -- a nozzle -- the blinding in a hole can be lost

(9) It is the ink constituent of the feature and either of (8) about the solvent of the aforementioned ink constituent being a non-proton nature annular polar solvent.

[0028] In case the ink constituent concerned of (9) distributes or dissolves stably and is applied by the ink-jet method, without spoiling the property of hole-injection material or luminescent material, the stable regurgitation of it becomes possible.

[0029] (10) The ink constituent of either (6) characterized by including a glycol-ether system acetic acid, or (9).

[0030] It not only can suppress dryness of ink, but according to the ink constituent concerned of (10), it can improve membrane formation nature.

[0031] (11) a lower alcohol -- less than [20wt%] -- the ink constituent of either (6) characterized by containing, or (10)

[0032] According to the ink constituent concerned of (11), in case it applies especially by the ink-jet method, it becomes possible to adjust surface tension and viscosity to a desired value, without spoiling the regurgitation nature of ink.

[0033] (12) The ink constituent of (6) characterized by the aforementioned ink constituent containing the mixture of the poly thiophene derivative and a polystyrene sulfonic acid as this hole-injection material including hole-injection material.

[0034] According to the ink constituent concerned of (12), in case it applies especially by the ink-jet method, ***** and membrane formation nature are excellent and it becomes possible to obtain a highly efficient hole-injection layer in an organic EL element.

[0035] (13) The ink constituent of (12) characterized by furthermore containing a silane coupling agent as a heat-curing agent.

[0036] If the ink constituent concerned of (13) is used, the hole-injection layer which does not cause compatibility with a luminous layer in an organic EL element by applying especially by the ink-jet method can be formed.

[0037] (14) The ink constituent of (6) characterized by the aforementioned ink constituent containing the precursor of poly (PARAFENIREMBINIREN) and its derivative as this luminescent material including luminescent material.

[0038] According to the ink constituent concerned of (14), it can consider as the green which was excellent in ***** at the time of applying especially to the ink-jet method, and membrane formation nature, and was excellent in the luminescence property in the organic EL element, or the ink constituent for red luminous layers.

[0039] (15) The ink constituent of (14) characterized by using what doped low-molecular coloring matter as the aforementioned luminescent material.

[0040] According to the ink constituent concerned of (15), it can consider as the green which was excellent in ***** at the time of applying especially to the ink-jet method, membrane formation nature, and the luminescence property, or the ink constituent for red luminous layers. [0041] The above (6) or the ink constituent of (15) can be suitably used in the formation process of a hole-injection layer or a luminous layer in the manufacture method of the organic EL element of (1) or (5), respectively.

[0042] Moreover, according to this invention, the highly efficient organic EL element obtained by the above-mentioned method is offered.

[0043]

[Embodiments of the Invention] Hereafter, the operation form of this invention is explained in detail.

[0044] It is the method of applying on the substrate which the ink constituent which made the solvent dissolve or distribute the hole-injection material which serves as the manufacture method of the organic EL element by the ink-jet method of this invention from the organic substance which forms an element, and the luminescent material which becomes a row from the organic substance is made to breathe out from an ink-jet head, for example, a transparent electrode is formed, and constitutes a pixel, and forming a luminous layer in a hole-injection layer row. According to this ink-jet method, detailed patterning can be performed simple in a short time, and multiple-color-izing is possible. Moreover, material is not made useless, even if it becomes the substrate of a large area, since what is necessary is just to apply the material of an initial complement to a required place.

[0045] The structure of the head for ink jets used for the organic EL element of this invention in the manufacture method is shown in <u>drawing 1</u> and <u>drawing 2</u>. The head 10 for ink jets concerned is equipped with the nozzle plate 11 and diaphragm 13 made from stainless steel, and both are joined through the batch member (reservoir plate) 15. between a nozzle plate 11 and diaphragms 13 — a batch — two or more ink rooms 19 and ****** 21 are formed of the member 15 The ink room 19 and the interior of ****** 21 are filled with the ink constituent of this invention, and the ink room 19 and ****** 21 are opening them for free passage through a feed hopper 23. furthermore, the nozzle for injecting an ink constituent from the ink room 19 in the shape of JIETO to a nozzle plate 11 — the hole 25 is formed the ink introduction for on the other hand supplying an ink constituent to the head 10 for ink jets at ****** 21 — the hole 27 is formed Moreover, on the field which counters the ink room 19 of a diaphragm 13, and the field of an opposite side, it is made to correspond to the position of the aforementioned space 19, and the piezoelectric device 29 is joined.

[0046] This piezoelectric device 29 is located between the electrodes 31 of a couple, and if it energizes, it will bend so that a piezoelectric device 29 may project outside. The capacity of the ink room 19 increases by this. Therefore, the ink constituent equivalent to a part for the capacity which increased in the ink room 19 flows through a feed hopper 23 from ****** 21. Next, if the energization to a piezoelectric device 29 is canceled, both this piezoelectric device

29 and the diaphragm 13 will return to the original configuration. since space 19 also returns to the original capacity by this — the pressure of the ink constituent of the ink room 19 interior — going up — a nozzle — an ink constituent spouts towards a substrate from a hole 25 [0047] in addition, a nozzle — the periphery of a hole 25 — the flight deflection of an ink constituent, and a hole — in order to prevent plugging, the ** ink layer 26 is formed namely, a nozzle — the ** ink layer 26 which consists of a nickel-tetrafluoroethylene eutectoid deposit as the periphery of a hole 25 is shown in drawing 2 is formed

[0048] In the manufacture method of the organic EL element of this invention, the ink constituent containing the hole-injection material which is made to breathe out from the aforementioned head for ink jets, and is used, or luminescent material has the following properties.

[0049] The viscosity of an ink constituent is 1 - 20 mPa-s preferably, and is 2 - 8 mPa-s especially preferably. When the viscosity of an ink constituent is less than 1 mPa-s, solid part concentration becomes [too little] and control of discharge quantity not only becomes difficult, but may be unable to form enough films. the case where 20 mPa-s is exceeded -- a nozzle -- a possibility that an ink constituent cannot be made to breathe out smoothly from a hole -- it is -- a nozzle -- it may be necessary to change the specification of equipment, such as enlarging a hole case [furthermore,] viscosity is large -- a part for solid [in an ink constituent] -depositing -- easy -- a nozzle -- the blinding frequency of a hole becomes high [0050] Moreover, the surface tension of an ink constituent is 20 - 70 mN/m preferably, and is 25 - 45 mN/m especially preferably. By making it the surface tension of this range, the flight deflection in the case of ink **** can be stopped. the ** time which breathes out an ink constituent since the wettability on the nozzle side of an ink constituent will increase, if surface tension is less than 20 mN/m -- an ink constituent -- a nozzle -- it may adhere to the circumference of a hole asymmetrically in this case, a nozzle -- in order that attraction may work between the affixes made into the constituent adhering to the hole, and how to breathe out, the so-called flight deflection which will be breathed out by the uneven force and cannot reach a target position arises, and an ink constituent is natural -- the frequency also becomes high Moreover, since the configuration of the meniscus in the nose of cam of a nozzle will not be stabilized if 70 mN/m is exceeded, control of the discharge quantity of an ink constituent and **** timing becomes difficult.

[0051] The contact angle to the material which constitutes the ** nozzle side which breathes out the ink constituent prepared in the head for ink jets is 30 degrees – 170 degrees preferably, and is 35 degrees – 65 degrees especially preferably. When an ink constituent has the contact angle of this range, the flight deflection of an ink constituent can be controlled and precise patterning becomes possible. Since the wettability to the material which constitutes the nozzle side of an ink constituent increases when this contact angle is less than 30 degrees, flight deflection arises like the case where it is surface tension, moreover, if it exceeds 170 degrees — an ink constituent and a nozzle — the interaction of a hole serves as the minimum, and since the configuration of the meniscus in the nose of cam of a nozzle is not stabilized, control of the discharge quantity of an ink constituent and **** timing becomes difficult

[0052] Flight deflection means that the position which the dot reached produces a gap of 50 micrometers or more to a target position here, when an ink constituent is made to breathe out from the aforementioned nozzle mainly — a nozzle — it generates by the case where the wettability of a hole is uneven, the blinding by adhesion of the solid component of an ink constituent, etc.

[0053] 0.01 - 10.0wt% of the solid part concentration of an ink constituent is desirable to the whole constituent, and is still more desirable. [0.1 - 5.0wt% of] If solid part concentration is too low, in order to obtain required thickness, the number of times of **** will increase and mass-production efficiency will become bad. Moreover, even if too high, viscosity becomes high and ***** is affected.

[0054] As for a part for the above-mentioned solid one, it is desirable for the vapor pressure in a room temperature to dissolve or distribute to at least one or more solvents of 0.005 – 50mmHg. using the solvent it is hard to become it dry — an ink constituent — a nozzle — it can dry with a hole and can prevent adhesion for thickening, condensation, and solid taking place However, in membrane formation process, since removal of a solvent is difficult, a solvent with which vapor pressure is less than 0.005mmHg(s) is not suitable.

[0055] As such a solvent, glycol-ether system acetic acids, such as non-proton nature annular polar solvents, such as gamma-butyrolactone, N-methyl pyrrolidone (NMP), 1, and 3-dimethyl-2-imidazolidinone (DMI) and its derivative, or carbitol acetate (CA), and butyl carbitol acetate (BCA), are mentioned. Solvents, such as CA and BCA, are effective also at the point of raising membrane formation nature.

[0056] On the other hand, although lower alcohols, such as a methanol (MeOH), ethanol (EtOH), and propyl alcohol, are effective in manufacture of surface tension and viscosity, since volatility is high, it is desirable that it is less than [20wt%].

[0057] In addition, the above-mentioned property is suitable also as a property of the electron hole transportation material which constitutes this layer in the case of forming an electron hole transporting bed in an organic EL element.

[0058] Hereafter, this invention is explained still in detail in accordance with an example.

[0059] (Example 1) An example 1 is related with the ink constituent for hole-injection layer formation applied by the ink-jet method in manufacture of an organic EL element.

[0060] PEDT which is the poly thiophene derivative as a hole-injection material in this invention (polyethylene dioxythiophene)

[0061]

[0062] PSS (polystyrene sulfonic acid) [0063]

[0064] ******* was used. These can be purchased from a Beyer company as BAITORONP. As a hole-injection material (or electron hole transportation material used as the material of an electron hole transporting bed), although the poly aniline, a porphyrin compound, a pyridine derivative, etc. are mentioned, it is the macromolecule which is thermally durable and BAITORON P which can be distributed to polar solvents, such as water, is suitable for the

ink-jet method. The ink constituent shown in Table 1 using BAITORON P was prepared. [0065]

[Table 1]

組成物	材料名	含有量(wt%)
正孔注入/輸送材料	PEDT/PSS(パイトロンP)(水分飲液)	7.25
	*	52.75
極性溶媒	メタノール	5
	イソプロピルアルコール	6
	1、3ージメテルー2ーイミダソリジノン	30
シランカップリング剤	ァーグリシジルオキシブロビルトリメトキシシラン	0.08

[0066] In order to prevent compatibility with a luminous layer, the said weight addition was carried out with the conductive polymer, using gamma-glycidyloxypropyl trimethoxysilane as a silane coupling agent which constructs a bridge by heat-treatment. The solid part concentration of a final ink constituent was 0.16wt(s)%.

[0067] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink **** nozzle side of the head for ink jets, *****, patterning nature, and membrane formation nature is shown in Table 2. The following methods estimated the physical property and **** property of an ink constituent.

[0068] Viscosity: The value in 20 degrees C was measured with E type viscometer.

[0069] Surface tension: Similarly the value in 20 degrees C was measured by the plate method.

[0070] Contact angle: It measured as a static contact angle on the material

(nickel-tetrafluoroethylene eutectoid plating hydrophobic layer) which constitutes the ink **** nozzle side of the head for ink jets.

[0071] **** property: The head for ink jet printers (Epson MJ-930C) was used. Flight deflection measured impact dispersion of the ink drop on the substrate when setting distance of a head and a substrate to 0.6mm. a nozzle — a part for solid [of the ink constituent which carried out continuation **** (frequency of 7200Hz) of the ink constituent, and deposited as blinding frequency of a hole] etc. — a nozzle — the hole carried out blinding and the time taken to result in the state where **** became impossible was measured

[0072] Patterning nature, membrane—formation nature: After breathing out to the test cell shown in drawing 3 (a) and (b) and removing a solvent in a room temperature and a vacuum, 200 degrees C (condensation, flat nature, etc.) of membraneous qualities of the film which heat—treated for 10 minutes and was formed were observed under the microscope among the atmosphere. A test cell has the pixel (40-micrometer pitch) which carried out opening of the 2-micrometer thick polyimide 40 formed on the ITO substrate 41 with the diameter of 30 micrometer. Performing consecutive processing of oxygen gas plasma and fluorocarbon gas plasma to ****** the polyimide front face used what hydrophilicity—ized ***** and the ITO front face. In addition, the aforementioned plasma treatment may be which atmosphere in a vacuum and the atmosphere. And the ink constituent 44 was breathed out from the ink—jet head 43 of ink—jet equipment 42 to opening, and the film was obtained and evaluated. A result is shown in the following table 2.

[0073]

[Table 2]

粘度 [mPa·s]	7.08
表面强力 [mN/m]	44.9
接触角[*]	65
目詰まり頻度 [seo]	>10000
飛行ばらつき [μm]	±20
パターニング性	
成以性	

[0074] As shown in Table 2, it was that to which ******, patterning nature, and membrane formation nature reach sufficiency and practical use level. In addition, the place during

composition of Table 1 (for example, the place which prepared the methanol (MeOH) and the constituent with which the addition of isopropyl alcohol (IPA) exceeds 20%, formed like the above, and was evaluated), or the place which prepared the constituent which did not add 1 and 3-dimethyl-2-imidazolidine (DMI), but was replaced with water, formed like the above, and was evaluated — the above — even if it fulfills a physical value, blinding has been started among **** by thirst of an ink constituent

[0075] (Example 2) An example 2 is related with the ink constituent for luminous layers. [0076] In this invention, poly (PARAFENIREMBINIREN) (PPV) was used as a green luminescent material.

[0077] as an organic compound which can form a luminous layer, the poly propine vinylenes, such as the poly alkyl thiophenes, such as PTV (poly (2, 5-thienylene vinylene)), PFV (poly (2, 5-FURIREN vinylene)), poly para-phenylene, and the poly alkyl fluorene, a pyrazoline dimer, a KINORI gin carboxylic acid, benzo pyrylium perchlorate, a benzo peeler NOKINO lysine, a phenanthroline europium complex, etc. mention other than PPV -- having -- these -- one sort -- or two or more sorts can be mixed and it What consists of a macromolecule organic compound also in these is desirable. A macromolecule organic compound is excellent in membrane formation nature, and the endurance of a luminous layer is very good. Macromolecule system material has broad flexibility on a molecular design, and the rational design of EL light emitting device is possible for it. Moreover, it has the band gap of a visible region, and comparatively high conductivity, and a conjugated-system macromolecule has such a remarkable inclination especially. As a luminous layer material, the precursor of the conjugated-system macromolecule which conjugates by the conjugated-system macromolecule itself or heating (membrane formation) is used. PPV or especially its derivative is desirable also in these. As a precursor of a PPV derivative, a MO-PPV (poly (2, 5-dimethoxy -1, 4-phenylenevinylene)) precursor, a CN-PPV (poly (2, 5-screw hexyloxy-1, 4-phenylene -(1-cyano vinylene))) precursor, etc. are mentioned. The precursor before conjugation (membrane formation) of PPV or its derivative is meltable to water or a polar solvent, and fits the pattern formation by the ink-jet method. Furthermore, PPV or its derivative has strong fluorescence, and since it is also the conductive polymer which the pi electron of a double bond has delocalized on a polymer chain, the thin film of PPV can function also as a hole-injection transporting bed, and can obtain a highly efficient organic EL element. [0078]

[Formula 3]

[0079] The ink constituent shown in Table 3 using the poly (PARAFENIREMBINIREN) precursor (water / MeOH=5/95 mixed solution) was prepared. Solid part concentration was 0.3wt(s)%. [0080]

[Table 3]

組成物	材料名	含有量 (wt%)
発光材料	PPV前駆体溶液 (1.5wd%) (水/メタノール=5/95 混合溶液)	20
種性溶媒	1、3ージメチルー2ーイミダゾリジノン	70
	ブチルカルビトールアセテート	10

[0081] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink **** nozzle side of the head for ink jets, ******, patterning nature, and membrane formation nature is shown in Table 4.

The same method as an example 1 estimated the physical property and **** property of an ink constituent. After ****, in the room temperature and the vacuum, membrane formation nature removed the solvent, among nitrogen-gas-atmosphere mind, 150 degrees C, is what was processed for 4 hours, and evaluated it.

[0082]

[Table 4]

乾度 [mPa·s]	3.21
表面張力 [mN/m]	37.6
接触角["]	56.6
目詰まり頻度 [sec]	>10000
飛行ばらつき [µm]	±25
パターニング性	0
成膜性	•

[0083] As shown in Table 4, it was that to which ******, patterning nature, and membrane formation nature reach sufficiency and practical use level. On the other hand, although it was satisfactory to ****** for example, when the ink constituent which replaced butyl carbitol acetate (BCA) with the glycerol was prepared and the same membrane formation and same evaluation as the above were performed or it replaced DMI by the dimethylformamide (DMF), luminous efficiency was low and also shifted the luminescent color to the short wavelength side. the case where he wants to make solid part concentration deeper than 0.3wt(s)% — a precursor solution — more than 20wt% — if it adds — a MeOH content — increasing — ink — becoming it dry — being easy — since flight deflection and blinding were produced, what ****(ed) and condensed the precursor solution was used

[0084] (Example 3) An example 3 is related with the ink constituent for luminous layers. [0085] In this example, what added the rhodamine 101 which is a low-molecular fluorochrome as a red luminescent material was used for the PPV precursor ink constituent used in the example 2.

[0086] The method of doping the fluorochrome of a low-molecular system can change the luminescence property of a luminous layer, for example, is very effective considering the improvement in luminous efficiency, or luminescence wavelength as a frog means. The high red of color purity and green luminescence can be obtained by the dope of a fluorochrome. [0087] As a fluorochrome used for a red luminous layer, DCM of laser coloring matter, a rhodamine or a rhodamine derivative, a perylene, etc. can be used. Since it is low-molecular, it is meltable to a solvent, and these fluorochromes have PPV etc. and good compatibility and formation of the uniform and stabilized luminous layer is easy for them. As a rhodamine derivative fluorochrome, Rhodamine B, the Rhodamine B base, rhodamine 6G, rhodamine 101 perchlorate, etc. are mentioned, for example, and two or more sorts of these may be mixed. [0088] Moreover, as a fluorochrome used for a green luminous layer, a Quinacridone, rubrene, DCJT(s), and those derivatives are mentioned. Like the above-mentioned red fluorochrome, since these fluorochromes are low-molecular, PPV etc. and compatibility are good meltable and formation of a luminous layer is easy for them to a solvent.

[0089] In this example, the ink constituent for red luminous layers shown in the following table 5 was prepared.

[0090]

[Table 5]

組成物	材料名	含有量 (wtil)
発光材料	PPV前駆体溶液 (1.5wt%)	20
	(水/メタノール=5/95 混合溶液)	I
	ローダミン101	0.0045
		前駆体固型分出
		1.5wt%
極性溶媒	1、3ージメチルー2ーイミダゾリジノン	70
	プチルカルビトールアセテート	10

[0091] The result which evaluated the viscosity of the above-mentioned constituent, surface tension, the contact angle to the material which constitutes the ink **** nozzle side of the head for ink jets, ******, patterning nature, and membrane formation nature is shown in Table 6. The same method as an example 2 estimated the physical property of an ink constituent and a **** property, and membrane formation nature.

[0092]

[Table 6]

粘度 [mPa·s]	3.27
表面張力 [mN/m]	37.4
接触角["]	60
目詰まり額度 [sec]	>10000
飛行ばらつき [μm]	±25
パターニング性	•
成腐性	•

[0093] As shown in Table 6, it was that to which ******, patterning nature, and membrane formation nature reach sufficiency and practical use level. the amount of dopes of a rhodamine 101 -- a PPV precursor -- receiving -- 1.5wt(s)% -- when it added, it was the most efficient and red luminescence was shown

[0094] (Example 4) An example 4 is related with the manufacture method of the organic EL element by the ink-jet method. <u>Drawing 4</u> shows the manufacturing process of the full color organic EL element of three colors.

[0095] While the transparent substrate 104 is a base material, it functions as a field which takes out light. Therefore, the transparent substrate 104 is chosen in consideration of the transparency property and thermal stability of light. As a transparent substrate material, although a glass substrate, transparent plastics, etc. are mentioned, for example, since it excels in thermal resistance, a glass substrate is desirable.

[0096] First, the pixel electrodes 101, 102, and 103 were formed on the transparent substrate 104. As the formation method, although photo lithography, vacuum deposition, the sputtering method, the metal-fog method, etc. are mentioned, for example, being based on photo lithography is desirable. As a pixel electrode, a transparent pixel electrode is desirable, and a tin oxide film, an ITO film, the multiple-oxide film of indium oxide and a zinc oxide, etc. are mentioned as a material which constitutes a transparent pixel electrode.

[0097] Next, the septum (bank) 105 was formed by the photosensitive polyimide, and it buried each above transparent pixel inter-electrode. Thereby, improvement in contrast, prevention of the color mixture of luminescent material, the optical leak from between a pixel and pixels, etc. can be prevented.

[0098] although it obtains, and it will not be limited especially if it is, organic materials, such as acrylic resin, an epoxy resin, and a photosensitive polyimide, are desirable, for example from the thing which have endurance to the solvent of EL material as a material which constitutes a septum 105 and for which—izing can be carried out [Teflon] by fluorocarbon gas plasma treatment You may be the laminating septum which made inorganic material, such as liquefied glass, the lower layer. Moreover, a septum 105 mixes carbon black etc. in the above—mentioned material, and is good also as a black resist. As the formation method of this septum 105, photo lithography etc. is mentioned, for example.

[0099] Just before applying the ink constituent for hole-injection layers (further electron hole transporting bed), continuation plasma treatment of the oxygen gas of the above-mentioned substrate and fluorocarbon gas plasma was performed. Thereby, ***** and an ITO front face are hydrophilicity-ized and a polyimide front face can perform wettability control by the side of the substrate for carrying out patterning of the ink-jet drop minutely. As equipment which generates plasma, it can use similarly with the equipment which generates plasma in a vacuum, or the equipment which generates plasma in the atmosphere.

[0100] Next, the ink constituent for hole-injection layers mentioned in the example 1 was breathed out from the head 110 (Epson MJ-930C) of ink-jet print equipment 109, and the patterning application was performed on each pixel electrodes 101 and 102 and 103. The solvent was removed on a room temperature and the conditions of 20 minutes after an application and among the vacuum (1torr), and the ink constituent for luminous layers mentioned in the examples 2 and 3 and the hole-injection layer 120 not dissolving were formed among the atmosphere after that with 200 degrees C (on a hot plate), and heat treatment for 10 minutes. Thickness was 40nm. Although each pixel formed the common hole-injection layer in this example, depending on the case, you may form using the hole-injection material (or electron hole transportation material) which was suitable for the luminous layer the whole luminous layer.

[0101] The ink constituent for red luminous layers furthermore mentioned in the example 3 and the ink constituent for green luminous layers mentioned to the row in the example 2 were applied to the pixel electrode 101 row in the shape of PATANIN on 102 through the hole-injection layer 120 top with the ink-jet method. After an application and among the vacuum (1torr), the solvent was made to remove and conjugate continuously with 150 degrees C and heat treatment of 4 hours among nitrogen-gas-atmosphere mind on a room temperature and the conditions of 20 minutes, and the red luminous layer 106 and the green luminous layer 107 were formed. Thickness was 50nm. The luminous layer conjugated with heat treatment is insoluble to a solvent.

[0102] According to this ink-jet method, detailed patterning can be performed simple in a short time. Moreover, it is possible by changing the solid part concentration and discharge quantity of an ink constituent to change thickness.

[0103] Moreover, before forming a luminous layer, you may perform continuation plasma treatment of oxygen gas and fluorocarbon gas plasma in the hole-injection layer 120. A fluorine ghost layer is formed on a hole injection or the electron hole transporting bed 120 by this, and ionization potential can offer the increase of hole-injection efficiency, and the organic high EL element of luminous efficiency by the bird clapper highly.

[0104] Subsequently, the blue luminous layer 108 was formed on the pixel electrode 103 through the red luminous layer 106, green luminous layer 107, and hole-injection layer 120 top. Thereby, it not only forms the three primary colors of red, green, and blue, but it can bury and carry out flattening of the level difference of a red luminous layer and the 106 green luminous layer 107, and a septum 105. Thereby, vertical inter-electrode short-circuit can be prevented certainly. By adjusting the thickness of a blue luminous layer, in a laminated structure with a red luminous layer and a green luminous layer, a blue luminous layer acts as an electron-injection transporting bed, and does not emit light blue.

[0105] It is not limited especially as the formation method of this blue luminous layer 108, but membranes can be formed also by the general spin coat method as a wet method, or the ink-jet method. In this example, the spin coat of the xylene solution of the poly dioctyl fluorene was carried out, and the blue luminous layer 108 of 45nm of thickness was formed.

[0106] The poly dihexyl fluorene which is otherwise the poly fluorene derivative as a blue luminous layer, and a copolymer with other polymerization machines are mentioned, and an organic compound with a blue fluorochrome or electron-injection transportation ability may be added.

[0107] As an organic compound which can form an electron-injection transporting bed, PBD, the OKISA diazole derivative of OXD-8 grade, DSA, an aluminum quinol complex, Bebq, a triazole derivative, an azomethine complex, a porphin complex, etc. are mentioned. [0108] Since a full color organic EL element can be formed by combining with other organic luminescent material used for an ink-jet method even if it is the luminescent material which is seldom suitable for an ink-jet method by forming two colors with an ink-jet method among organic luminous layers, and forming other Isshiki by the conventional method of application like

10/11 2003/11/26 14:13

this example, the flexibility of an element design increases. As the conventional methods of application other than an ink-jet method, print processes, a replica method, a dipping method, the spin coat method, the cast method, the capillary-tube method, the roll coat method, the bar coat method, etc. are mentioned.

[0109] Finally, cathode (counterelectrode) 113 was formed. As cathode 113, a metal thin film electrode is desirable, and Mg, Ag, aluminum, Li, etc. are mentioned as a metal which constitutes cathode, for example. Moreover, the alloy which can use a small material of a work function other than these, for example, contains alkali metal, alkaline earth metal, such as calcium, and these can be used. Moreover, a metaled fluorine ghost can also be adapted. Such cathode 113 can be formed by the vacuum deposition, the spatter, etc. In this example, calcium was carried out by the vacuum heating vacuum deposition, 1200nm laminating of the 100nm of the aluminum was further carried out by the spatter, and it considered as cathode.

[0110] Furthermore, you may form a protective coat on cathode 113. By forming a protective coat, cathode 113 and degradation of each luminous layers 106, 107, and 108, damage, exfoliation, etc. were able to be prevented.

[0111] As a component of such a protective coat, an epoxy resin, acrylic resin, liquefied glass, etc. are mentioned. Moreover, as the formation method of a protective coat, the spin coat method, the casting method, a dipping method, the bar coat method, the roll coat method, the capillary—tube method, etc. are mentioned, for example.

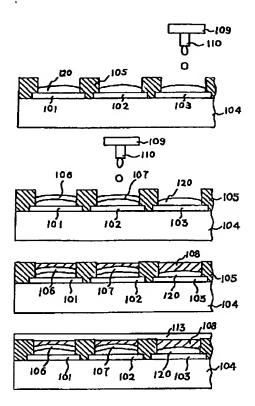
[0112] In the organic EL element obtained by this example, two or more 100 cd/m brightness was obtained [the low battery not more than 5V] for the pixel of each color. Moreover, in the red pixel and green pixel which were formed with the ink-jet method, luminous efficiency was 0.15 lm/W and 0.25 lm/W, respectively, and the luminescence life (time when continuation luminescence is carried out, until it impresses fixed current, and it falls 50% to initial brightness) was also 2000 hours or more.

[0113] It was of the same grade as the thing of the red light emitting device which formed the hole-injection layer and the luminous layer by the same laminated structure on the spin coat using the same material as the above, and a green light emitting device. Thus, the property which was excellent also in the ink-jet method was able to be shown, and the element which is not inferior to a spin coat article was able to be formed.

[Translation done.]

2003/11/26 14:13

Drawing selection [R presentative drawing]



Copyright (C); 2000 Japan Patent Office

JAPANESE [JP,2000-323276,A]	
	TECHNICAL FIELD PRIOR ART EFFECT OF THE MEANS DESCRIPTION OF DRAWINGS DRAWINGS
[Translation done.]	

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the flat-surface perspective diagram showing an example of the structure of the printer head for ink jets used for manufacture of the organic thin film EL element of this invention.

[Drawing 2] It is the cross section showing an example of the structure of the nozzle portion of the printer head for ink jets used for manufacture of the organic thin film EL element of this invention.

[Drawing 3] In the example of this invention, it is drawing showing the patterning nature of an ink constituent, and the test cell used for membrane formation nature evaluation.

[Drawing 4] It is the cross section showing an example of the manufacture method of the organic EL element of this invention.

[Description of Notations]

- 10 Head for Ink Jets
- 11 Nozzle Plate
- 13 Diaphragm
- 15 Batch -- Member
- 19 Ink Room
- 21 *****
- 23 Feed Hopper
- 25 Nozzle -- Hole
- 26 ** Ink Layer
- 27 Ink Introduction -- Hole
- 29 Piezoelectric Device
- 31 Electrode
- 33 Nozzle Side
- 40 Polyimide Septum
- 41 ITO
- 42 Ink-Jet Print Equipment
- 43 Ink-Jet Head
- 44 Ink Constituent
- 101 Pixel Electrode (Red)
- 102 Pixel Electrode (Green)
- 103 Pixel Electrode (Blue)
- 104 Transparent Substrate
- 105 Septum
- 106 Luminous Layer (Red)
- 107 Luminous Layer (Green)
- 108 Luminous Layer (Blue)

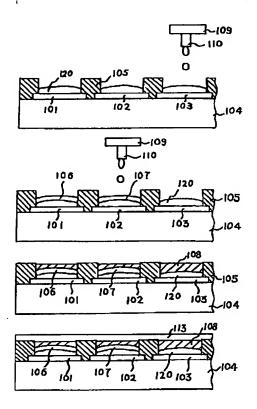
109 Ink-Jet Print Equipment

110 Ink JIETO Head

113 Cathode

120 Hole-Injection Layer

Drawing selection [Representativ drawing]



Copyright (C); 2000 Japan Patent Office

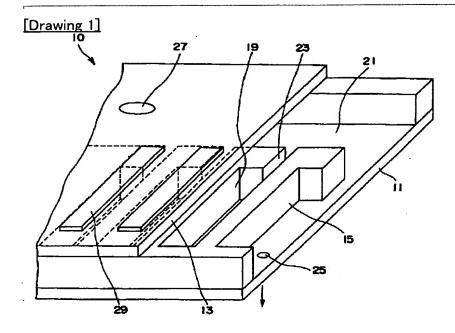
CLAIMS DETAILED	DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
	ICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

* NOTICES *

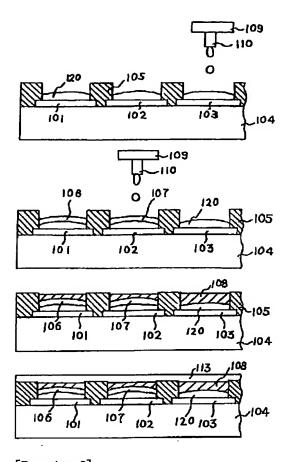
Japan Patent Office is not responsible for any damages caused by the use of this translation.

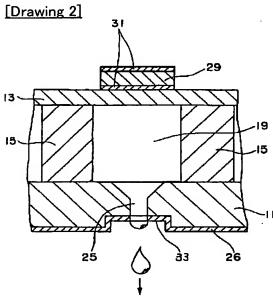
- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS



[Drawing 4]

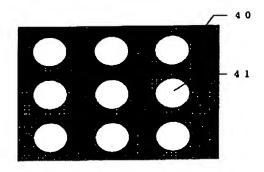


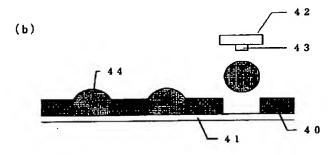


[Drawing 3]

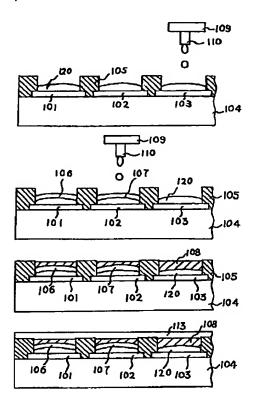
2003/11/26 14:16

'(a)





Drawing selection [R pr sentativ drawing]



Copyright (C); 2000 Japan Patent Office

(19) 日本国格部庁 (JP)

公 被 (v) 盐 华 噩 4 32

(11)特許出國公開番号

特開2000-323276

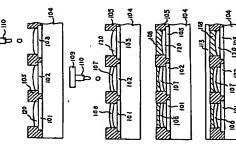
平成12年11月24日(2000.11.24) (P2000-323276A) (43)公開日

(51) In. C.7 (494)				
10 5 B 33/10 3 K 0 3 K	(51) Int.Q.	40000	FI	テーマコート・(各本)
9/80 365 G09F 9/80 365B 5C0 33/14 A 33/14 A 33/14 A 33/14 A 33/14 A 33/12 Z 2 #査論報: 未開來 開來現の概念 OL (全 #立即中5月14日(1999.5.14)	H05B3	3/10		
33/12 B 33/12 B 33/14 A 33/22 Z 2 33/14 A 33/22 Z 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2				365B
33/72 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2		3/12		
10 10 10 10 10 10 10 10	m	3/14	33/1	14 A
第空間次 未開北 間が現の数28 OL (全 原平11-13-4520 (71)出版人 000072363 中イコーエブソン様式会社 東文都新信区西新信 2 T 目 4 番 1 4 (72)発明	83	3/22	32/58	22
(71) 出版人 000072369			警查翻求 为	k階水 開水項の数28 OL (全 12 頁)
中点11年5月14日(1999, 5.14) 東京都部自区西新市2丁目4毎14 (72)発明者 岡 使一 長野県東部市大和3丁目3番5号 ーエブソン株式会社内 (72)発明者 ホロ 治史 長野県東部市大和3丁目3番5号 ーエブソン株式会社内 (72)発明者 ホロ 治史 長野県東部市大和3丁目3番5号 ーエブソン株式会社内 (74)代理人 100088888	(21) 出版事号	11年11-134320	(11) 出版人 (1	. 69820000
平成11年5月14日(1999.5.14) 東京都部自区西新市2丁目4番14 (72)発明者 四 使一 長野保護助市大和3丁目3番5号 ーエブソン株式会社内 (72)発明者 ホロ 治史 長野保護助市大和3丁目3番5号 ーエブソン株式会社内 (74)代理人 100088888			+º	アイローエゲンン株式会社
四 使一 長野県駅市大和3丁目3番5号 ーエブソン株式会社内 木口 治史 長野県駅市大和3丁目3番5号 ーエブソン株式会社内 100083388 押強士 館木 喜三郎 (外2名)	(22) 出版日	平成11年5月14日(1999.5.14)	**	5京都新宿区西新宿2丁目4番1号
長野県駅坊市大和3丁目3番5号 ーエブソン株式会社内 本口 治安 長野県駅坊市大和3丁目3番5号 ーエブソン株式会社内 10008388 井陸士 鈴木 喜三郎 (外2名)				- B
ーエブンン株式会社内 本口 治史 長野県駅市大和3丁目3番5号 ーエブンン株式会社内 100083388 井陸士 鈴木 喜三郎 (外2名)			*A	5野県諏訪市大和3丁目3番5号 セイコ
本口 治史 長野県駅市大和3丁目3番5号 -エブンン株式会社内 100083388 井陸士 鈴木 喜三郎 (外2名)			_	-エブソン株式会社内
長野県駅坊市大和3丁目3巻5号 -エブンン株式会社内 10008388 井陸士 鈴木 草三郎 (外2名)				が 日本
ーエブソン株式会社内 100093388 弁理士 鈴木 暮三郎			arts.	5野県諏訪市大和3丁目3番5号 セイコ
100093388 井理士 65木 春三郎			1	- エブンン株式会社内
的木 專三郎				886226000
			***	的木 專三郎
				最終頁に依く

(54) 【発明の名称】 有種EL様子の包造方法、有種EL様子およびインク組成権

[限盟] 有機薄膜EL類子の簡便かつ容易な製造方法を ぬ女すること。 (57) [政権]

持した構造の有機EL囃子の製造方法であって、基板上 の所定の関域に有機化合物からなる正孔注入材料を含む インク組成物をインクジェット方式により資布し正孔在 入層 (120) を形成する工程と、有機化合物からなる 発光材料を含むインク組成物をインクジェット方式によ 9 独布し発光層(106、107)を形成する工程とを [解決手段] 正孔注入图 (120) と発光層 (106、 耳臼することを整数とする。



存置2000-323276

3

2.系酢酸を含むことを特徴とする請求項6乃至9のいず 【語火斑10】 哲配イング組成物がグリコーゲエーデ れかに記載の有機EL囃子の製造方法。

で牧村した構造の有様EL珠子の製造方法でもって、基

「請求項1】 正孔往入層と発光層を、間極および陰極

凡住入層を形成する工程と、有機化合物からなる発光材

含むインク組成物をインクジェット方式により塗布し正 料を含むインク組成物をインクジェット方式により強布 J発光層を形成する工程とを具備することを特徴とする

坂上の所定の倒域に有機化合物からなる正孔注入材料を

20wt%以下含むことを特徴とする請求項6乃至10 「諸求項11】 前配インク組成物が短級アグローグを のいずれかに記載の有機EL辮子の製造方法。

むものであり、蚊正孔往入材料としてポリチオフェン醇 グ剤を含有することを特徴とする請求項12配載の有数 [請求項12] 前記インク組成物が正孔柱入材料を含 海体とポリスチレンスケフォン数の配合物を合むことを [請求項13] 更に転頭化剤としてシランカップリン 特徴とする諸水項6記載の有機圧し架子の製造方法。 2

[請求項2] 前配有機EL囃子が基板上に複数の画類

自様EL業子の製造方法。

役け、核隔壁間の領域に前配正孔注入層及び前配発光層 を形成することを特徴とする請求項1配載の有機EL寮 【請求項3】 前配有機EL架子が甚板上に複数の画架 を有する栞子であり、基板上に歓画栞毎を隔てる隔壁を

子の製造方法。

を有する葉子であり、基板上に数画葉毎を隔てる隔壁を

のかもり、奴略光材料とした、 ポリ (パラクェニアンガ **ニレン)およびその税単体の前駆体を含むことを特徴と** 【請求項14】 前記インク組成物が発光材料を含むも トる請求項 6 記載の有機EL囃子の製造方法

EL 菓子の製造力符。

プしたものを使用することを特徴とする請求項14配畝 「耐水項15」 前配発光材料として低分子色架をドー の有機EL囃子の製造方法。

の連続処理工程を経て、前配正孔注入層と、前配発光層

毀け、酸鞣ガスプラズマとフロロカーボンガスプラズマ

を形成することを特徴とする請求項1配載の有機EL寮

子の製造方法。

【請求項4】 前配有機化合物からなる正孔注入材料を 後、蚊インク組成物の溶媒を除去して、正孔注入層を得 ンク組成物をインクジェット方式により塗布した後、数 インク組成物の溶媒を除去し、発光圏を得ることを特徴 [請求項5] 前配有機化合物からなる正孔柱入材料を 後、さらに熱処理により数インク組成物の材料を硬化あ **るいは共役化させて正孔往入層を得ること、及び前配有**

含むインク組成物をインクジェット方式により塗布した

ること、及び前配有機化合物からなる発光材料を含むイ

[請求項16] 請求項1乃至15のいずれかに配載の 方法により製造される有機巨し報子。

[請求項17] 有機EL群子の製造においてイングジ エット法により塗布される、正孔住入材料又は発光材料 ヘッドのノズル旧を構成する材料に対する扱動角が30 を含むインク組成物であって、粘度が1~20mFa・ s、牧面投力が20~70mN/m、インクジェット

[請求項18] 固型分撥度が0.01~10.0wt %であことを特徴とする請求項17記載のインク組成 ~170° であることを特徴とするインク組成物。

ន

含むインク組成物をインクジェット街により独布した

とする請求項1記載の有機EL菜子の製造方法。

(宮温) の少なくとも一種の容媒を含むことを特徴とす |課失極19| | 核気圧が0.001~50mmHg

> インク組成物の材料を硬化あるいは共役化させて発光階 を得ることを特徴とする請求項1記載の有機EL類子の 【請求項6】 前配正孔住入材料又は前配務光材料を含 むインク組成物の粘度が1~20mPa·s、数面張力

以治力社。

ジェット方式により強布した後、さらに熱処理により厳

機化合物からなる発光材料を含むインク組成物をインク

「請求囚20」 有配インク結成をの路域が非プロトン **社費状極性溶媒であることを整徴と請求項19記載のイ** 5請水垣17又は18記載のインク組成物。

(請求項21) 前記グリコールエーテル系酢酸を含む ことを特徴とする請求項17乃至20のいずれかにイン ソク組成物。 40

ル面を構成する材料に対する接触角が30~170°で

が20~10mN/m、インクジェットヘッドのノズ

あることを特徴とする請求項1乃至5記載のいずれかに [請求項7] 前記インク組成物の固型分譲度が0.0 1~10.0wt%であることを特徴とする請求項6配

記載の有機EL類子の製造方法。

(請求項22] 低級アルコールを20wt%以下含む ことを特徴とする請求項17乃至21配鉱のインク組成 ク組成物。

[静水頃23] 前配インク組成物が正孔柱入材料を含 ひものであり、歓圧孔在入材料としてポリテオフェン醇 単体とポリスチレンスルフォン数の風合物を含むことを

[請求項24] 更に熱硬化剤としてシランカップリン グ剤を含有することを特徴とする請求項17記載のイン 特徴とする請求項17記載のインク組成物。

ය

~50mmHg (室温) の少なくとも一種の溶媒を含む 「請求項9】 前記インク組成物の路域が非プロトン性 **環状極性溶媒であることを特徴とする請求項8配載の有**

ことを特徴とする請求項6又は7配畝の有機EL架子。

[静水項8] 前記インク組成物の蒸気圧が0.001

戦の有機区1群子の製造方法。

【部水坂25】 前記インク組成物が現光対料を合むらのであり、原発光対料とした、ボリ(ベウンェニアンドニソン)およびその認識体の態度体を合むにとを特徴さる語彙なして記載のインク組成物。

「膝状虫26】 前四発光対応として弱分子色媒をドープレたものを使用することを特徴とする諸状母26記載のインク組成物.

[発明の詳細な説明]

[0001] [発明の属する技術分野] ディスプレイ、表示光線など に用いられる電気的発光等子である存機区上等子の製造 方法、有機区上 菓子、その正孔柱入層や発光層の形成に 用いられるインク組成物に関する。 【従来の技術】近年液晶ディスプレイに着わる自発電光 型ディスプレイとして発光層に右接物を用いた発光算中の開発が加速している。右接EL(エレクトロルミキセンス) 環子における有複物からなる発光層の形成プロセスとして、Appl. Phys. Lett. 51 (12)、21 September 1987の913ページに示されているように低分子材料を整物法で成原する方法と、Appl. Phys. Lett. 71 (11)、7 July 1997の34ページや5声を [0003] カラー化の手段としては低分子系材料を用いる始合、所定パターンのマスク超しに異なる第光色の智光材料を所留の回葉対応が高分に形なし形成する方形が行われている。一方、成分子承材料を用いる場合・微細かつ容易にパターニングができることからインクジェット社を用いる機と 基子の作製については、例えば、特別平7-235378、特別平10-12377、特別平11-64270に開示されている。

【0004】さらに右接EL類子では、独光効率、耐分性を向上させるために、正孔住入衛または正孔線送衛を 路径と発光周の間に形成することが境がされている(A ppl. Phys. Lett. 51、21 Septe nbor 1987の913ページ)。従来、パップケ の中正孔住入届としては導配性高分子、例えばポリチオフェン誘導体やパリアーリン誘導体(Nature, 3 57, 477、1992)を用い、スピンコート等の強布性により競技形成する。低分子が材料の正孔柱入衛または正孔構造圏として、フェニルアミン誘導体を搭着でたほ正孔構造圏として、フェニルアミン誘導体を搭着で 【発明が好決しようとする課題】有機臣し第子において、正孔住入層及び発光層の積層構造を形成する際に、 50

正孔柱入層及び発光層を構成する有機薄膜を材料を無駄 にせず、簡便にかつ微細にパターニングして成膜する手

段が要求されている。

る。これら刊行他では出出社の点からDMF (ジメチル ンピニレン (PPV)を用いる場合、PPV 前原体と共 【0006】インクジェット方式は大変有効である。し ンク組成物の閲覧は大変難しい課題である。有機EL琛 **-40358、特朗平11-54270に記載されてい** ホルムアミド) や歯楓剤としたグリセリンやジエチレン グリコール毎の高沸点容媒を使用した組成物が記載され ている。DMFは熱、酸、アルカリに対する安定性に関 高級アルコールは緑色発光材料としたポリパラフェニレ かし材料の特性を損なわずに機能限として成駁できるイ 困があり、グリセリンやジエチレングリコールといった かし、インクジェット掛による安定な吐出性を摘たし、 役化の過程で反応し特性を阻害してしまう問題がある。 また、特にグリセリンは除去するのが困難である。 2

[0001]また、パターニングの分解能を上げるため、ノズル箆を小さくし、より小さなイングジョット液液を形成しようとすると、液液が小さくなればなるほとインクは乾きやすくなるといった閻圀も生じている。

[0008] さらに、インクジェット社のみならず塗布 在で有機器を指揮する場合、組成物の溶媒が下地器の有機膜を溶解する、いわゆる相容性が問題となる。具体的 には正孔往入層(または正孔輸送階)の上に発光器を形

れているように高分子材料を塗布する方法が主に開発さ

れたいる。

[0009] そこで本発明の限題とするところは、簡便、短時間、低コストで神性の優れた有機関語以からなる有機とし第子を製造する方法ならびにそれを可能にするインク組成物を提供するところにある。

成する組合である。

シェンン Maxing RR からし、シェンにおう。[0010](課題を解決するための年段] 本籍明によれば、下記

る。 【0011】 (1) 正孔注入層と発光層を、陽極および

(1) ~ (5) の有機EL類子の製造方法が提供され

降極で独特した権途の有機でし事子の製造方法であって、基板上の所定の倒転に有機化合物からなる正孔柱入 材料を含むインク組成物をインクジェット方式により箇 布し正孔柱入価を形成する工程と、有機化合物からなる 現光材料を含むインク組成物をインクジェット方式により 現光材料を含むインク組成物をインクジェット方式により 込油し発光価を形成する工程とを具備することを特徴 とする有機EL 排子の製造方法。

[0012] 当嫁方法は有機化台物からなる正孔性入層及び発光層の両方をイングェット方式で形成したものである、かかる方法により、所便な方法で全ての有機屬を形成することができ、またいずれの層も高い性能とすることができる。

· 【0013】尚、本発明において、正孔柱入層とは、協 50 極関から発光層に有効に正孔を注入させ得る層であり、

正孔輪送機能をも有する。また、正孔柱入層と共に、正 孔輪送機能を有する正孔輪送陽を別局で飲けてもよい。 [0014](2)有機に上解すか益成上に被愛國解 を有する架子であり、基板上に韓國報在を掲てる隔壁を 飲け、蘇城壁間の領域に前配正孔柱入層及び前配発光層 を形成することを特徴とする(1)の有機を上類子の製 格方法。

[0015]当版(2)の方法により、現なる発光面が 組合することなく、多色で且の返措面の右機区し班子を 容易に得ることができる。 (0016) (3) 有機EL架子が基板上に拡製の回簿を有する架子であり、基板上に貸回架毎を届てる税でを関け、酸菜ガスプラズマとフロロカーボンガスプラズマの道側が埋工題を経て、前配正孔注入層と前配務光層を形成することを特徴とする(1)の有機EL類子の製造

【0017】当覧(3)の方法により、基反上に演演の節れ性の違いを付与することができ、インクジェント液形の資品をクラーニングが可能となる。

[0018] (4)前部石機化合物からなる正孔法入材料を含むインク組成物をインクジェット方式により邀拾した後、数インク組成物の石様を除せして、正孔柱入配を除ること、及び前記有機化合物からなる現光材料を含むインクジェット方式により強布した後、数インク組成物の石様を除出し、発光値を得ることを特徴とする(1)の右機臣に対予の製造方法。[0019]当数(4)の方法により所図の特性の正孔柱入局及び発光層としての有機固体環膜を形成するによ

[0020](5)前配右機化合物からなる正孔性入材料を含むインク組成物をインクジェット誌により盤布した後、さらに繁処理により酸インク組成物の材料を現代あるいは共役化させて正孔柱入間を得ること、及び前配有機化合物からなる発光材料を含むインク組成物をインクジェット方式により塗布した後、さらに緊処理により数インク組成物の材料を現化あるいは共役化させて発光質を得ることを特徴とする(1)の有機EL類子の製造

方法。 【0021】当隊(5)の方法により、優れた機能を有 する正孔往入層および発光層を形成できる。

[0022]また、本独明によれば、下記(6)乃至(15)のインク組成物が提供される。(6)右提臣し 雅子の製造においてイングェット荘により強布される正元往入材料文は発光材料を含むインク組成物であって、粘度が1~20mPa・s、数面扱力が20~70mN/m、イングジェットヘンドのノズル面を構成する材料に対する復独角が30~170。であることを特徴とするインク組成物。

【0023】当数(6)のインク組成物によれば、特に インクジェット法により塗布する場合に、ノズル孔の目

参照2000-323276

Ŧ

結まり、インク液液の保行曲がりを押さえるとともに吐出を円光にし、吐出量および吐出タイミングの原因が可能となり、イングの原因が可能となり、インクジェット方式による安定な吐出が可能した。

【0024】(7)固型分資度が0.01~10.0wt%でおことを特徴とする(6)のインク組成物。【0025】当算(7)のインク組成物によれば、インクジェット符により塗布する場合に、は出性を損なうことなく所図の原原を得ることが可能となる。

10 [0026] (8) 株気圧が0.001~50mmHg (細菌)の少なくとも一種の溶媒を含むことを容散とする(6)又は(7)のインク組成物。

[0027] 当版(8) のインク組成物によれば、インクジェットにより資布する際に、インクの塩きを抑えることができ、ノズル孔での目前まりをなくすことができ、ノズル孔での目前まりをなくすことができ

(9) 前配インク組成物の溶媒が岩プロトン柱盤状菌性溶媒であることを特徴と(8)のいずれかのインク組成溶媒であることを特徴と(8)のいずれかのインク組成物

20 【0028】当版(9)のインク組成物は、正孔柱入材料をおおいは発光材料の物性を損ねることなく、安定に分散まれば溶解し、インクジェット注により資布する際に安定な出出が可能となる。

 【0030】当類(10)のインク組成物によれば、インクの配きを抑えることができるだけでなく、成項性を向上することができるだけでなく、成項性を向上することができる。

30 [0031] (11) 極級アルコールを20wt%以下 名むことを特徴とする(6) 乃至(10) のいずれかの インク組成物。 [0032] 当版 (11) のインク商成的によれば、移にイングメント形により強告する際に、インクの出出 在を扱わることなく数面扱力および特質を所図の国に関額することが可能となる。

(0031)(12) 神智インク組成物が正光柱入材料 か合むものであり、凝正光柱大材柱としてボリケギフェン超過杯とボリスチレンメンマンマンを設成とよびスチレンスケン・2段の低台物を合むこのとを整数とする (6)のイング組成物。

とを等数とする(6)のインク組成物。 【0034】当数(12)のインク組成物によれば、移 にインクジェット街により飽布する際に、吐出性、成駁 性ともに優れ、有機EL母子において高柱能の正孔柱入

届を得ることが可能となる。 【0035】(13)叉に熱硬化剤としてジランカップ リング剤を含在することを特徴とする(12)のインク [0036]当数(13)のインク組成物を用いれば、 特にインクジェット出により数布することで、有機EL 60 算子において我光陽との相談を起こさない正別在入陽を

むものであり、飯鴉光材料として、ポリ(パラフェニレ [0037] (14) 前記インク組成物が発光材料を含 ンアニレン)およびその税当体の哲野体を合むことを特 取とする(6)のインク盤成物、

[0038] 当数 (14) のインク組成物によれば、特 れ、有機EL架子において発光物性の優れた緑色または **にインクジェット部に独布する駅の出出柱、成数柱が像 歩色発光層用イング組成物とすることができる。**

2 [0039] (15) 前配発光材料として低分子色報を ドープしたものを使用することを特徴とする (14)の

[0040] 当数 (15) のインク組成物によれば、特 にインクジェット荘に迯布する際の吐出性、成模性およ の発光物性の優れた緑色または赤色発光層用インク組成 物とすることができる。 ムソケ結成を。

は、夫々、(1)乃至(5)の有機EL衆子の製造方法 における正孔住入届や発光層の形成工程において好適に 【0041】上記(6)乃至(1.2)のインク組成物 用いることができる。

[0042]また、本発明によれば、上記方法により得 られた、高性能の有機EL菓子が協供される。

ន

[0043]

【発明の契頼の形態】以下、本路明の契約形態にして

は描に説明する。

トヘッドから吐出させて倒えば随即気極が形成され画群 [0044] 本発明のインクジェット方式による有機臣 し栞子の製造方法とは、栞子を形成する有機物からなる 正孔注入材料、ならびに有機物からなる発光材料を溶媒 **に溶解または分散させたインク組成物を、インクジェン** を構成する基板上に登布し、正孔柱入層ならびに発光層 を形成する方法である。 かかるインクジェット方式によ とができ、多色化が可能である。また、必要な場所に必 **要量の材料を塗布すればいいので大面積の基板になって たば、独描なパターニングを簡便にむり囲時間で行うこ** も材料を無駄にすることは無い。

ゴスケンフス製のノズルプレート11と被動板13とを ンク 盆 19 からインク組成物をジェト状に増射するため [0045] 本発明の有機ELサ子に製造方法において 使用されるインクジェット用ヘッドの構造を図1および 図2に示す。当該インクジェット用ヘッド10は、例え 四文、両者は仕切部材(リザーパープレート)15を介 して協合されている。ノズルブレート11と被制板13 との間には、仕辺部材15によった複数のインク国19 おり、インク国19と液留り21とは供給ロ23を介し **のノズル孔25が散けられている。一方、インクジェッ** 液揺り21の内部は本発明のインク組成物で描たされて **ト湖油したこる。からに、ノダクプワート11には、イ**

板動板13のインク室19に対向する面と反対側の面上 には、前記空間19の位置に対応させて圧電索子29が するためのインク導入孔21が形成されている。また、 接合されている。

る。したがって、インク宝19内に増大した容積分に相 [0046] この圧電票子29は一対の電極31の間に 位置し、通電すると圧電架子29が外側に突出するよう に越曲する。これによったインク留19の容徴が増大す 当するインク組成物が液溜り21から供給ロ23を介し て流入する。次に、圧恒架子29への通電を解除する

る。これにより空間19も元の容積に戻るためインク室 19内部のインク組成物の圧力が上昇し、ノズル孔25 と、蚊圧電栗子29と複動板13はともに元の形状に戻 【0047】なお、ノズル孔25の周辺部には、インク から基板に向けてインク組成物が噴出する。

ク層26が設けられている。すなわち、ノズル孔25の 周辺部は、図2に示すように例えばNiーテトラフルオ 因成物の飛行曲がり、孔詰まりを防止するために撥イン ロエチレン共析メッキ層からなる撥インク層26が設け られている。

C、 世間インクジェット用ヘッドから外出させて用いる 正孔住入材料、あるいは発光材料を含むインク組成物は [0048] 本発明の有機臣上囃子の製造方法におい 以下のような特性を有するものである。

[0049] インク組成物の粘度は好ましくは1~20 である。インク組成物の粘度が1mPa・s未満である 母合、吐出量の制御が困難になるばかりでなく、固型分 20mPa・sを超える場合、ノズル孔からインク組成 mPa・sであって、特に好ましくは2~8mPa・s **物を円滑に吐出させることができない恐れがあり、ノヌ** ル孔を大きくする等の装置の仕様を変更する必要が生じ ることがある。更に粘度が大きい場合、インク組成物中 の固型分が折出し易く、ノズル孔の目詰まり頻度が高く 潑度が過少となり十分な膜を形成できないことがある。

8

ことになり目棋位置に到達できない所謂飛行曲がりが生 ご、もちろんその復既も高くなる。また、70mN/m を超えるとノズル先端でのメニスカスの形状が安定しな る。 牧西蝦力が20mN/m米荷であると、インク組成 いたやインク 植成物の中田曲、中田タイミングの制御が 45mN/mである。この範囲の装面扱力にすることに より、インク吐出の豚の飛行曲がりを抑えることができ 物のノズル面上での隠れ性が増大するため、インク組成 **あを吐出する際、インク組成物がノズル孔の周囲に非対** た組成物と吐出しようとする付着物との相互間に引力が 働くため、インク組成物は不均一な力により出出される [0050]また、インク組成物の数面扱力は好ましく は20~10mN/mでむって、毎に好ましくは25~ **木に付着することがある。この場合、ノズル孔に付着し**

\$

困難になる。

ය

ト用ヘンド10には、液焰り21にインク組成物を供給

た。170。を超えると、インク組成物とノメル孔の相 ク組成物を吐出するノズル面を構成する材料に対する投 かのノズル固を構成する材料に対する語れ性が協大する 互作用が極小となり、ノズル先端でのメニスカスの形状 [0051] インクジェット用ヘッドに敷けられたイン 性角は好ましくは30。~170。であり、特に好まし くは35。~65。 でわる。 インク結成物がいの衛田の 段触角を持ついとによって、インク組成物の既行曲がり を制御することができ、精密なパターンニングが可能と なる。この接触角が30。未微である場合、インク組成 こめ、 按面視力の場合と同様、 飛行曲がりが生じる。 ま が安定しないためインク組成物の吐出曲、吐出タイミン グの制御が困難になる。

【0052】ここで低行曲がりとは、インク組成物を相 が、目標位置に対して50μm以上のずれを生じること ンク組成物の固型成分の付着による目詰まり等によって をいう。主にノズル孔の個れ性が不均一である胡合やイ 記ノメルから吐出させたとき、ドットの着弾した位置

ន 【0053】インク組成物の固型分譲度は、組成物全体 と必要な核厚を得るために吐出回数が多くなってしまい ~5.0wt%が更に好ましい。固型分換度が低すぎる **田蔵効率が悪くなってしまう。また高すぎても粘度が高** に対して0.01~10.0×t%が好ましく、0.1 くなったしまい引出祖に宏勢を与える。

は分散していることが望ましい。 渇きにくい溶媒を用い [0054] 上記固型分は室温での蒸気圧が0,005 ~50mmHgの少なくとも一つ以上の容媒に容解また **ることによりインク組成物がノズル<u>孔で乾</u>燥し、増粘、**

【0062】とPSS(ポリスチレンスルフォン殻) [0063]

特別2000-323276

9

しかし、蒸気圧がの.005mmHgを下回るような容 * 極棋、固型分の付着が起こることを防ぐことができる。 **媒は、成膜過程で溶媒の除去が困難であるため適さな**

チルー2ーイミダソリジノン(DMI)およびその菸導 ルアセテート (CA)、プチルカルビトールアセテート (BCA) などのグリコールエーテル系酢酸が挙げられ る。CA, BCA等の溶媒は成版性をわげる点でも有効 [0055] このような铬煤としては、γープチロラク **存などのおプロトン柱段状協在路接、またはカルアトー** トン、N-メチルピロリドン (NMP)、1、3-ジメ 2

ルは安面扱力、粘度の閲覧に有効であるが、揮発性があ ゲ(EtOH)、プロピルアルコーグ母の南級アルコー [0056] 一方、メタノール (MeOH) 、エタノー いため、20wt%以下であることが留ましい。

正孔輸送層を形成する場合の同層を構成する正孔輸送材 [0057] 尚、上近の犂供は、有機足し蚦子において 【0058】以下、本格則を実施例に拾って更に幹値に 本の移在としても辞過である。

【0059】 (状态例1) 状态例1は右茲EL母子の以 **遊においてインクジェット法により登布する正孔柱入層** 形成用インク組成物に関する。

[0060] 本発明では、正孔住入材料として、ポリチ **ギレェン税単谷でもるPEDT(ポリエチアンジオキツ**

[0061]

[42]

* む、水などの梅性溶媒に分散できるバイトロンPがイン

クジェット方式には適している。パイトロンPを用いて

数1に示すインク組成物を調製した。

[0064] の混合物を用いた。これらはパイトロンP としてパイエル社から購入することができる。正孔注入 材料(又は正孔輸送層の材料となる正孔輸送材料)とし ては、ポリアニリン、ポケフィリン化合物、ピリジン税 導体などが挙げられるが、釈的に耐久性のある高分子

[0065]

最後	材料名	台有量 (wt
五九七人一种没有种	PED1/PSS(パイトロンP) (水分散液)	7.25
	*	52.75
報の登録	W-16x	\$
	イソプロピルブルコール	2
	1、3ージメデルー2ーイモダンリジノン	83
アンカップリング報	し つがらられませんプロピハナリメトキシミッシュ	90'0

हा ।

オキシプロピルトリメトキシシランを用い、導電性高分 子と同血量欲加した。及称的なインク組成物の固型分類 [0066] 発光周との相容を防ぐため、加釈処理によ 0 保値するシランカップリング剤としてゝーグリシジル 度は0.16×1%であった

性を評価した結果を示す。インク組成物の物理的性質お クジェット用へッドのインク吐出ノズク面を構成する杖 **料に対する被触角、吐出性、パターニング性および成駁** [0067] 数2に上記組成物の粘度、数面扱力、イン

ន

【0068】 粘度: E型粘度計により 2 0 ℃における値 よび出出等性にしてれば下の方法が詳値した。

[0069] 牧団般力: ブレート部により同じく20℃

における値を測定した。

【0010】 敬勉角: インクジェット用ヘッドのインク **吐出ノズル面を熔成する材料 (Niーテトラフルオロ**

[0071] 吐出物性: インクジェントプリンター用へ ッド (エブソン社製M J - 930C) を用いた。 飛行曲 エチレン共折メンキ版木碣)上での静的接触角として遡 がりはヘッドと基板の距離を0.6mmにした時の基板

上でのインク液液の均容にのつきを刨庇した。ノメル孔 の目詰まり頻度として、インク組成物を連続吐出(周抜 数7200Hz) し、折出したインク組成物の固型分類 によりノズル孔が目詰まりし、吐出不能になった状態に 至るまでに要する時間を測定した。

媒を除去した後、大気中200℃、10分割処理して形 を用いた。尚、前記プラズマ処理は其空中、大気中のい 【0012】パターニング性、成敗性:図3 (a) 及び (b) に示したテストセルに吐出し、笛祖、其空中で符 成された頃の頃質(騒痕、平坦性等)を顕微鏡で観察し テストセルはITO 基板41上に形成した2 um 平 ポリイミド40を30ヵ日紹で既口した国珠(40ヵ日 ピッチ)を有するものである。吐出前に、酸珠ガスプラ ポリイミド校面は撥水化、ITO牧面は殻水化したもの ずれの雰囲気かめってもよい。 そした、インクジョット 装置42のインクジェットヘッド43からインク組成物 ズマとフロロカーボンガスプラズマの連続処理を行い、

2に示す。

[0073] [聚2]

H)、インプロピルアルコール (IPA) の液均量が2 0%を超える組成物を閲覧して上記回袋に成膜し、評価 リジン(DMI)を添加せず木で置き換えた組成物を調 **製して上記回様に成駁して評価したところ、上記物理的** 【0014】数2に示すように、吐出性、パターニング したところ、または、1,3ージメチルー2ーイミダン な値を描たしても、インク組成物の渇きにより吐出中、 **性、成既性とも十分、実用レベルに強するものであっ** た。尚、数1の組成中例えば、メタノール (MeO 8

【0075】 (契施例2) 契施例2は発光層用インク組 目詰まりを起こしてしまった。

成物に関する。

【0076】本発明では、緑色発光材料としてポリ (パ ラフェニレンピニレン) (PPV)を用いた。

P P V の街に、 P T V (ポリ (2、5 - チェニアンアニ 【0011】発光層を形成し得る有機化合物としては、 レン)) 毎のポリアルキルチオフェン、PFV (ポリ (2、6-レリフンガニフン))、 ポリベアレョニフ ソ、よリアグキケングギョン韓のよりアリフンピニフ

\$

能である。また、可視倒転の禁止帯幅と比較的高い導電 上幅広い自由度を持ち、EL発光索子の合理的設計が可 性を有しており、なかでも共役系高分子はこのような優 向が顕著である。発光隔材料としては、井役系高分子そ が好ましい。高分子有機化合物は成膜性に優れ、発光層 の耐久性は極めて良好である。高分子来材料は分子設計 ン、ピランリンダイヤー、キノリジンカグボン酸、ベツ る。 これらのなかでも高分子有機化合物からなるもの ソピリリウムペークロレート、ペンンピラノキノリジ ン、フェナントロリンユウロピウム錯体等が挙げられ、 これらを1種または2種以上混合して用いることができ

ය

4.4を閉口部に吐出し紋を得て評価した。 結果を下配数

* 哲野体は、大もろいは極柱路核に巨路でもり、 インクジ P P Vまたはその税簿体は強い蛍光を持ち、二重結合の でもあるためPPVの辞棋は正孔往入輸送層としても機

参照2000-323276

⊛

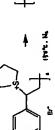
ェット方式によるパターン形成に適している。さらに、

* 向子がポリケー数上で非国在化している導向性電分子

能し、高性能の有機EL辮子を得ることができる。

[0078]

られる。PPVまたはその秘導体の共役化(成駁) 前の* のもの、あるいは加熱等により共役化 (成膜) する共役 **条高分子の前駆体が用いられる。これらのなかでもPP** 竹駅体として、MO-PPV(ポリ(2、5-ジメトキ ツー1、4ーレョリフンカリフン)) 哲啓存、CNーP PV (ポリ (2、5ーピスヘキシルオキシー1、4ープ **ェニンソー(1ーシアノアニフン)) 性勢存得が特別** Vまたはその誘導体が特に好ましい。 PPV誘導体の



[0800] ※わせりた。 (水/WeOH=5/95概合格液)を用いて数3に示 【0079】 ポリ(パテフォニアンアニアン) 色路存

₩3] すインク組成物を調製した。固型分換度は0.3wt%%

	5 H H	54 X (WO)
表光柱草	PPV的關係學孫 (1.5md)	8
	(水ノメタノール=5/95 張台海流)	
国性お菓	1、3-ジメチル-2-43がカジバン	20
	ブチルカルピトールアセチート	10

料に対する接触角、吐出性、パターニング性および成膜 性を評価した結果を示す。インク組成物の物理的性質お た。成敗性は吐出後、望福、其空中で路媒を除去し、蛮 [0081] 数4に上配組成物の粘度、数面視力、イン クジェット用ヘッドのインク中田ノズク固を権成する女 よび 出事性に しょ ては 東極 別 1 と 回接 の 方法 で 評価 し **寮雰囲気中、150℃、4時間処理したもので評価し**

[0082]

12.8	37.6	56.6	>1000	∓32	0	0
記憶 [mPa・m]	食団狙力 [mV/m]	事を無し	日指宋リ凱鹿 [800]	飛行ばらつき [μm]	がん(ニーを)/	東部位

【0083】数4に示すように、吐出性、パターニング ころ、吐出性に固固はなかったが、殆光効率が低く、発 光色も短波長側にシフトしたものであった。固型分撥度 ミド (DMF) で置き換えたあるいは、プチルカルビト を0.3wt%より強くしたい場合は、前駆体溶液を2 0wt%以上添加するとMe OH台有量が増え、インク -ルアセテート (BCA) をグリセリンで置き換えたイ ンク組成物を調製し上配同様の成膜及び評価を行ったと た。これに対し、例えば、 DMIをジメケルホルムア 性、成膜性とも十分、実用レベルに達するものであっ が褐きやすくなり、飛行曲がりや目詰まりを生じるた め、前原体容液を溜去して強縮したものを用いた。

[0084] (契約例3) 契約例3は発光階用インク組

[0085] 本契約例では、安約例2で用いたPPV前 邸体インク組成物に赤色路光材料として低分子蛍光色紫 **であるローダミン101を設加したものを用いた。** 成物に関する。

発光層の発光特性を変化させることができ、例えば、発 光効率の向上、または発光故長をかえる手段として大変 [0086] 低分子琴の歯光色群をドープする方符は、 右殆である。歯光色数のドープにより色核既の境い部 色、緑色発光を得ることができる。

は、フーチー的母のDCMもるいはローダミンせたはロ り、PPV等と相路性がよく、均一で安定した路光層の ミン6G, ローダミン101過塩素酸塩等が挙げられこ **ーダホン税当存、ペリフン毎を用いるいとができる。い** は、例えばローダミンB,ローダミンBペース、ローダ 【0087】 痧色箱光層に用いられる蛍光色群として れらの蛍光色繋は、低分子であるため溶媒に可溶であ 形成が容易である。ローダミン院導体蛍光色繋として 4

しては、キナクリドン、ルブレン、ロCJTおよびそれ 【0088】また、緑色発光層に用いられる蛍光色築と ちの誘導体が挙げられる。これらの蛍光色漿は、上配券 色蛍光色雅と同様、低分子であるため铬煤に可容であ れらを2種以上成合したものであってもよい。

9、またPPV毎と相容性がよく発光層の形成が容易で

[0089] 本契范例では、下記数5に示す砂色殆光層 用インク組成物を閲覧した。

[0600] 09

[聚5]

の発音	材料名	華早春
先先科科	PPV数単体治法 (1.5mg) (木/メタノール=5/96 四合语法)	ន
	D-52:101	0.004
		日共日本
		Sarch
を存む場	1.3ージメチルー2ーイモダブリジバン	9
	プチルカルピトールアセ アー ト	01

#65

ş

クジェント用ヘッドのインク吐出ノズル面を構成する材 科に対する彼独角、吐出性、パターニング性および成成 在を評価した格米を示す。インク組成物の物理的社質お よび早田等性、 政政性については映版例2と国核の方法 [0091] 投6に上配組成物の粘度、安面扱力、イン かな笛した。

[0092]

(発色)

ន

[0093] 数6に示すように、吐出性、パターニング ローダミン101のドープ曲はPPV前原体に対し 1. Bwt%菘加した雄合、もっとも効率よく、赤色発 **4、成成性とも十分、契用レベルに迫するものであっ**

ができる。

のフルカラー有機EL架子の製造工程を示したものであ [0094] (契粞例4) **契粞例4はインクジェット**方 式による有機EL類子の製造方法に関する。図4は3色

光を取り出す面として被能する。従って、強明基板10 る。透明基板材料としては、例えばガラス基板、透明プ ラスチック等が挙げられるが、耐熱性に優れることから [0095] 通明基板104は、支持体であると同時に 4は、光の超過特性や配的安定性を考慮して顕択され ガラス基板が好ましい。

1、102、103を形成した。形成方法としては、例 えばフォトリングラフィー、真空落着、スパッタリング **ィーによることが好ましい。 画祭句格としたは郊野画祭** [0096]まず、強明基板104上に、画雑電極10 **花、パイロンが拍母が治げられるが、フォトリングラフ** は、嬰化スメ版、I TO版、嬰化インジウムと酸化曲鉛 気極が好ましく、逸明画琳覧極を構成する材料として との複合酸化物膜等が挙げられる。

ミドで形成し、上記の各強明画森電極間を埋めた。これ によりコントラストの向上、発光材料の磁色の訪止、画 **【0097】次に風雪 (パンク) 105を感光性ポリイ** なと画なとの問からの光色れ等を防止することができ

ಜ

等を低入してブラックレジストとしてもよい。この隔壁 シ柑脂、戯光性ポリイミド等お有機材料が好ましい。 液 【0098】 **医翌105を権成する材料としては、** EL 材料の路媒に対し耐久性を有するものえあれば特に限定 されないが、フロロカーボンガスプラズマ処理によりテ フロン化できることから、例えばアクリル樹脂、エポキ 状ガラス等の無機材料を下層にした積層隔壁であっても よい。また、風豊105は上記材料にカーボンブラック 105の形成方法としては、例えばフォトリングラフィ 一等が挙げられる。 2

[0099] 正孔柱入層 (更に正孔輸送層) 用インク組 **ーポンガスプラズトの連続プラズト処理を行った。これ** れ、インクジェット液液を微細にパターニングするため の基板側の隔れ性の制御ができる。プラズマを発生する 成物を塗布する直前に、上記基板の酸薬ガスとフロロカ によりポリイミド牧画は榎木化、ITO牧画は蜺木化さ 大気中でプラズマを発生する装置でも同様に用いること 装置としては、真空中でプラズマを発生する装置でも、

た(ホットプレート上)、10分の敷処理により、実施 が、場合によっては各発光層毎で発光層に適した正孔柱 【0100】女に、契紘例1で挙げた正孔住入昭用イン 110 (H///分類製M J-930C) から早出し、4 画珠亀版101、102、103上にパターニング資布 分という条件で溶媒を除去し、その後、大気中、200 例2、3で挙げた発光層用インク組成物と相容しない正 ク組成物をインクジェットプリント装置109のヘッド を行った。 塾布後、耳空中(1torr)、 室温、20 孔柱入層120を形成した。 関厚は40mmであった。 入材料(または正孔輸送材料)を用いて形成しても良 本実施例では各画業とも共通の正孔注入層を形成した ຂ

ク組成物をインクジェット方式により正孔注入層120 塩、20分という条件で容媒を除去し、続けて登粜雰囲 発光層106、緑色発光層101を形成した。膜厚は5 【0101】さらに実施例3で挙げた赤色発光隔用イン ク組成物、ならびに実施例2で挙げた緑色発光層用イン 上を介して回葉電極101ならびに102上にパターニ 気中、150℃、4時間の敷処理により共役化させ赤色 0nmであった。熱処理により共役した発光層は溶媒に ン状に数布した。数布後、真空中 (1 torr)、 室 不容である。

9

[0102] かかるインクジェット方式によれば、街笛 る。また、インク組成物の固型分徴度および吐出量を変 なパターニングを簡便にかり短時間で行うことができ えることにより膜厚を変えることが可能である。

20に酸素ガスとフロロカーボンガスプラズマの連続プ ラズマ処理を行ってもよい。これにより正孔柱入または 正孔輸送層120上にフッ弊化物層が形成され、イオン 化ポテンシャルが高くなることにより正孔往入効略が始 [0103]また、発光層を形成する前に正孔柱入層1 し、発光効率の高い有機EL鞍子を提供できる。

ショートを確実に防ぐことができる。骨色発光層の膜厚 び106緑色発光層107と隔壁105との段差を埋め を調整することで、背色発光層は赤色発光層および緑色 発光層との復層構造において、電子柱入輸送層として作 06、緑色発光層107および正孔柱入層120上を介 て平坦化することができる。これにより、上下電極間の [0104] 次いで、育色発光層108を赤色発光層1 録、青の3原色を形成するのみならず、赤色発光層およ して画雑覧権103上に形成した。これにより、歩、 用し、青色には発光しない。 【0105】かかる育色発光層108の形成方法として **法またはインクジェット法でも成駁可能である。本実施** 別では、ポリジオクチルフルオレンのキシワン格液をス ピンコートして、駁厚45mmの背色発光層108を形 **は咎に版定されず、値式符として一般包なメアンコート**

【0106】 育色発光陌としては街にポリングオレン駅 導体であるポリジへキシルフルオレンや、その他の組合 基との共宜合体が挙げられ、青色蛍光色粱や電子注入輪 **送能をもつ有機化合物を添加してもよい。**

【0107】電子往入輸送層を形成し得る有機化合物と しては、PBD, OXD-8等のオキサジアゾール税当 体、DSA、アルミキノール錯体、Beba、トリアン **一々愁導存、アンメチン館存、ポケレィン館存存が浄げ**

をインクジェット方式により形成し、他の一色を従来の 式に用いられる他の有機発光材料と組み合わせることに 【0108】本実核例のように、有機発光層のうち2色 急布方法で形成することにより、インクジェント方式に もまり適さない発光材料であっても、インクジェット方 よりフルカラー有機EL菜子を形成することができるた め、栗子散計の自由度が増す。インクジェット方式以外 の従来の独布方法としては、印刷法、既写法、ディッピ ング荘、スピンコート荘、キャスト荘、キャピラリー 、ロークコート社、ベーコート社体が挙げられる。

い材料を用いることができ、例えばアルカリ金属や、C た。 路極113としては金属薄膜電極が好ましく、路極 を構成する金属としては、例えばMg、Ag、A1、L 1 毎が挙げられる。また、これらの他に仕事閲数の小さ 【0109】最後に、韓福(対向臨極)113を形成し

a等のアルカリ土類金属およびこれらを含む合金を用い このような路極113は蒸着法およびスパック法等によ ることができる。また金属のファ群化物も適応できる。 特開2000−323276

り形成することができる。本実施例では、Caを其空加 熱な者法で100nm、さらにAIをスパッタ法で12

び各発光图106、107、108の劣化、損傷および もよい。保護限を形成することにより、特徴113およ **【0110】さらに格極113の上に保護限を形成して** 00nm復居して路径とした。

慰痛等を防止しすることができた。

[0111] このような保護限の構成材料としては、エ る。また、保護膜の形成方法としては、例えばスピンコ **しト啎、キャスティング缶、ディッピング缶、パーコー** ト法、ロールコート法、キャピラリー法母が挙げられ **ポキン樹脂、アクリル樹脂、液状ガラス等が巻げられ**

色の画葉とも5V以下の低低圧でも100cd/m2以 [0112] 本契施例で得られた有機臣し類子では、各 上の輝度が得られた。また、インクジェット方式により 光寿命(一定電流を印加し、連続発光させた協合、初期 ■度に対し50%低下するまでの時間)も2000時間 形成した赤色画葉、緑色画葉においては、発光効中がそ れぞれ0. 151m/W、0. 251m/Wでわり、路 以上であった。 ន

[0113] 上記同様の材料を用い、スピンコートで正 孔住入局および発光層を同じ積層構造で形成した赤色発 し、メピンコート品に劣らない琳子を形成することがで 光芽子、緑色発光紫子のものと同程度であった。このよ うに、インクジェット方式においても優れた特性を示

[0114]

[発明の効果] 以上本発明によれば、正孔柱入層及び発 易迅速に有機EL辮子を得ることができる。また、吐出 ット方式により正孔住入または正孔輸送層および発光層 **か簡便かり容易にスターン形成でき、簡陥構造からなる** 特性の優れた店補細フルカラー有機EL辮子を製造する 光陌の回方をインクジェット荘で形成し、低コストで簡 性、パターニング性および成膜性に優れた正孔柱入用イ ンク組成物および発光材層用インク組成物を協供するこ とができた。また、数インク組成物を用い、インクジェ

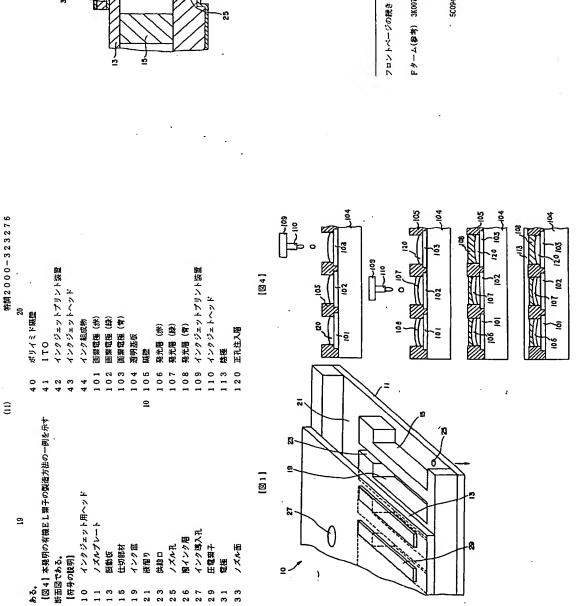
ことができる。

[図1]本発明の有機薄膜Eし架子の製造に用いられる **パンクジェット用プリンターヘッドの構造の一倒を示す** [図画の簡単な説明] 平面斜視図である。

[図2] 本発明の有機薄膜EL菓子の製造に用いられる **パンクジェット用プリンターヘッドのノズル部分の核治** 5 一色を示すを用図させる。

[図3] 本発明の実施例において、インク組成物のパタ **ーニング性、成膜性評価に用いるテストセルを示す図で**

S



3

>/

特開2000-323276

(13)

[⊠3]

[82]

3

Fターム(参考) 3K007 AB03 AB04 AB18 CA01 CA05 CB01 DA00 DB03 EB00 FA00 . 5C094 AA05 AA08 AA24 AA43 BA27 CA23 EA05 EB02 GB10 FA01 FA03